

# FINAL REPORT

Hybrid Ultra-Low VOC and Non-HAP Rain Erosion Coatings

SERDP Project WP-2603

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## **List of Acronyms**

<b>Symbol</b>	<b>Meaning</b>
AA	Aluminum Alloy
AF	Air Force
AFRL	Air Force Research Laboratory
ASTM	American Society for Testing and Materials
ATR	Attenuated Total Reflectance
COTS	Commercial Off the Shelf
DI	Distilled Ionized
DOD	Department of Defense
EHS	Environmental Health and Safety
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared Spectroscopy
GC	Glycidyl Carbamate
GE	General Electric
HAP	Hazardous Air Pollutant
HDI	Hexamethylene Diisocyanate
IDPI	Isophorone Diisocyanate
MEK	Methyl Ethyl Ketone
MIBK	Methyl Isobutyl Ketone
MPK	Methyl Propyl Ketone
MW	Molecular Weight
NIPU	Non-isocyanate Polyurethane
NDSU	North Dakota State University
OEM	Original Equipment Manufacturer
QUV	Q-Panel Laboratory Ultraviolet
SBIR	Small Business Innovative Research
STTR	Small Business Technology Transfer
TBAC	Tertiary Butyl Acetate
UTS	Ultimate Tensile Strength
VOC	Volatile Organic Compound
USAF	United States Air Force

## **Keywords**

1. Rain Erosion
2. Leading Edge Erosion
3. Radome Protection
4. Protective Coating
5. Glycidyl Carbamate
6. Non-isocyanate Polyurethane
7. Low Volatile Organic Content (VOC)

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## **1.0 Abstract**

### ***1.1 Objective***

Numerous military aircraft and shipboard surfaces, such as radomes, antennas, gun shields, wing leading edges, and helicopter blade leading edges, are coated with a specialized erosion-resistant protective coating possessing strict performance requirements. These protective coatings must provide excellent rain erosion resistance, superior mechanical properties, good adhesion to the substrate and meet a host of other metrics outlined in MIL-PRF-32239 and SAE AMS-C-83231A. Historical protective coatings that meet these metrics are often polyurethane-based and contain large quantities of volatile organic compounds (VOCs), hazardous air pollutants (HAPs), and isocyanates which are hazardous and may be prohibited for use in the near future under the Prohibited and Controlled Chemical List (PCCL). A drastic reduction in VOCs, HAPs, and other hazardous compounds in such coatings will lead to significant environmental and occupational safety improvements, as well as increased coating application productivity associated with reduced application and cure times. Protective tapes, an alternative to rain erosion protective coatings, have recently been developed to reduce applicator occupational safety hazards; however, these tapes have shown a drastic decrease in performance compared to conventional coating systems. Currently no wear resistant coating or tape alternative can meet the desired requirements for VOCs, HAPs, and isocyanates while meeting the performance metrics under MIL-PRF-32239A and SAE AMS-C-83231A.

The objective of Luna's limited scope program was to develop a rapid curing rain erosion coating that has low VOC content and is non-HAPs via the use of exempt solvent technologies. Luna's goal was to develop a rain erosion coating based on a unique glycidyl carbamate (GC) hybrid resin chemistry that offers epoxy-type rapid reactivity and adhesion combined with excellent erosion, flexibility, weathering, and mechanical properties typical of polyurethane systems.

### ***1.2 Technical Approach***

Luna focused on coating chemistry and full formulation development followed by property validation per MIL-PRF-32239A and SAE AMS-C-83231A, including rain erosion testing. Variants were initially screened for erosion performance using a custom ultrasonic cavitation test method developed by Luna. Other key metrics that were tested include impact resistance, low temperature flexibility, dry/wet adhesion, elongation, and tensile strength. Luna assessed top performing coatings for application time, coating buildup, and cure time prior to full rain erosion testing at the University of Dayton Research Institute per SAE AMS-C-83231A requirements.

### ***1.3 Results***

The limited scope program was enabled by the completion of several individual tasks that culminated in the demonstration of highly flexible GC coating variants. The Luna team synthesized and formulated a variety of resins and coatings intended to bolster the toughness and impact resistance over prior GC coatings by optimizing the resin chemistry, investigating new curative packages, and carefully selecting additives for toughness and durability. To date, Luna's efforts have resulted in several formulations that show excellent flexibility, adhesion, and impact

resistance and are comparable to a commercial rain erosion coating system. The program demonstrated that there is significant room to create GC-based environmentally-friendly rain erosion systems and reduce risk associated with hazardous materials during coating application. Additional work will be needed to optimize coatings for rain erosion performance and future funding will allow Luna to move the technology from the development phase toward SAE AMS-C-83231A qualification and full DoD transition.

#### ***1.4 Benefits***

With a successful ultra-low VOC and non-HAP rain erosion coating, the return-on-investment for SERDP and the DoD agencies (e.g., the USAF) in terms of lowered sustainment and environmental costs associated with radome protective coatings on aircraft will be significant. This is associated with the large quantity of USAF and Navy aircraft radomes and antennas processed annually at maintenance depots. Other commercial markets include leading edges of military and civilian aircraft wings, hypersonic missiles, lift rockets and spacecraft, wind turbine blades, and helicopter blade leading edges. The application market is extremely widespread. Luna will leverage existing internal contacts for collaboration with the USAF, UDRI, aircraft depots, Prime integrators, and coating manufacturers to facilitate DoD transition

## 2.0 Objective

This effort focused on rain erosion coating chemistry and full formulation development followed by extensive property validation. The objective of the project was to develop GC-based coating systems and acquire the data necessary to demonstrate proof-of-concept via validation testing (e.g. rain erosion) against requirements in SAE AMS-C-83231A<sup>1</sup>. With additional follow-on work and funding to optimize a GC system, the return-on-investment (ROI) for SERDP and the DoD agencies (e.g. the USAF) in terms of lowered sustainment and environmental costs associated with radome protective coatings on aircraft will be significant. This is associated with the large quantity of C-130, F-16, F-15, KC-135, and B-52 radomes processed annually, and is not limited to only radomes. Other commercial markets include leading edges of military and civilian aircraft wings, hypersonic missiles, lift rockets and spacecraft, wind turbine blades, and helicopter blade leading edges. The application market is extremely widespread for the developmental technology.

### 2.1 *Limited Scope Program Technical Objectives*

The objective of the program was to demonstrate the feasibility of producing a rapid curing rain erosion coating system that has low VOC content, is non-HAPs via the use of exempt solvent technologies, and does not contain free isocyanates. Luna worked to acquire the data necessary to demonstrate proof-of-concept via validation testing (e.g. rain erosion testing) against requirements in SAE AMS-C-83231A, thereby proving efficacy for a possible follow-on SERDP project focused on coating optimization, scale-up, and transition to the USAF and other DoD agencies. A detailed description of the limited scope project technical objectives is given below.

#### **Objective 1 – Formulate rain erosion coating systems based on GC technology with low VOC and non-HAP materials**

Rain erosion coatings were formulated using Luna's GC resin technology. The original goal of this objective was to develop a full coating system consisting of a pretreatment; a primer having excellent adhesion, corrosion protection, hydrolytic stability, and impact resistance; and a topcoat optimized for rain erosion protection, UV stability, and rapid cure/recoat capability. Early in the program, it was decided to focus development on a GC rain erosion topcoat to reduce formulation complexity and enable more coating formulation/test iterations. Luna prepared numerous GC topcoat variants for evaluation as part of this objective. In separate efforts under Air Force Phase I/II STTR (FA9550-09-C-0150, completed 2010)<sup>2</sup> and Phase I SBIR (FA8650-16-M-5063, completed 2017)<sup>3</sup>, Luna developed a flexible non-chromate GC primer that has the potential to be integrated into the full rain erosion coating configuration.

#### **Objective 2 – Demonstrate the coatings meet base relevant performance specification requirements**

Throughout formulation development, topcoats were evaluated against metrics in SAE AMS-C-83231A and MIL-PRF-32239A<sup>4</sup>. Topcoats, which provide a majority of the erosion protection in DoD qualified rain erosion coating configurations, were screened using methods under SAE AMS-C-83231A and MIL-PRF-32239A including impact resistance, low temperature flexibility, and dry/wet adhesion. Additional testing included the evaluation of mechanical properties such as ultimate tensile strength (UTS) and elongation at the UTS. The best performing topcoat variants were screened via a custom ultrasonic cavitation method developed by Luna and final formulations were evaluated on the AFRL Rain Erosion Test Apparatus operated by the



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University of Dayton Research Institute (UDRI).<sup>5</sup> The primary success metric of this objective was to demonstrate at least one coating chemistry/system that exhibited performance comparable to existing COTS rain erosion coatings. While Luna was not able to meet or exceed existing COTS coating performance, sufficient data was collected to provide guidance on how to optimize such coatings based on the GC chemistry in follow-on work.

**Objective 3 – Demonstrate technology efficacy via rain erosion testing**

Down selected topcoats were tested by UDRI for rain erosion resistance on a specialized test rig in accordance with SAE AMS-C-83231A requirements. Up to 18 distinct Luna coating variants were applied to glass fiber composite airfoil substrates for testing. Comparison testing was also performed on an SAE AMS-C-83231A qualified COTS rain erosion system. While none of the Luna coatings met or exceeded the COTS performance during rain erosion testing, they incorporated significantly lower amounts of VOCs and no free isocyanates compared to the COTS product and sufficient data was collected to provide further guidance on an optimization pathway for GC based coating chemistries in future work.

### **3.0 Background**

The following sections provide a detailed background on rain erosion coating technology and the primary technology focus area during the limited-scope program.

#### ***3.1 Historical Rain Erosion Coatings for Aircraft***

Military coating systems are typically comprised of a chemical pretreatment applied directly to the substrate for protection against corrosion and enhanced primer adhesion, an organic primer for additional corrosion protection and improved topcoat adhesion, and an organic topcoat that meets specific performance objectives for the appropriate service environment. Primer systems on aircraft typically protect the integrity of the underlying metallic substrate through a combination of corrosion prevention and corrosion mitigation techniques while topcoats provide a barrier to the ingress of water and other corrosion initiating compounds. Additionally, topcoat systems provide weathering resistance of the underlying substrate and prevent coating degradation from mild impact events (water, sand, debris) and UV light. Traditional topcoats are suitable for many aircraft applications, however, susceptible areas such as leading edges and radomes require additional protection of the underlying substrate (aluminum, fiber reinforced composites) to prevent catastrophic rain erosion events. Urethane-based rain erosion topcoat systems are commonly used on platform regions that encounter high velocity impact with water droplets. These impact events are significantly damaging to common urethane and/or epoxy topcoat systems based on their high impact energy and erosive nature. Specialty formulations are thus required to survive such continual service in high velocity rain conditions and these coatings are usually controlled and specified by SAE AMS-C-83231A<sup>1</sup> or MIL-PRF-85322C<sup>7</sup>.

Numerous COTS systems meet the requirements of MIL-PRF-85322C for polyurethane rain erosion coatings. Under MIL-PRF-85322C, coatings must meet a range of performance metrics, contain less 420 g/L of VOC content, and pass 30 minutes of rain erosion testing on a qualified test apparatus. Additionally, polyurethane based coatings must meet specific physical properties, including a minimum UTS of 1000 psi and a minimum elongation at break (UTS) of 350% as determined by ASTM D2370. For example, Lord Corporation produces the Aeroglaze M1433A/B and Chemglaze M331/M201 rain erosion products that meet MIL-C-85322C standards, however both are polyurethane systems that contain free isocyanate compounds.

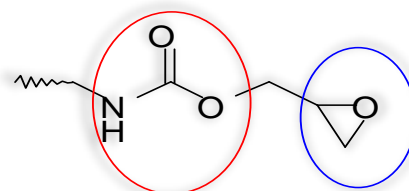
Under SAE AMS-C-83231A, coatings must meet similar performance metrics but have the ability to withstand 150-180 minutes on a qualified test apparatus with no limitation on VOC content. There are currently no physical performance requirements under SAE AMS-C-83231A in terms of UTS or minimum elongation at break (UTS). Examples of two DoD authorized rain erosion products that currently meet the requirements of SAE AMS-C-83231A, include the B-274 coating system from CAAP and the HC05XP1 coating system from Hontek.<sup>6,8</sup> Both the B-274 and HC05XP1 systems are based on isocyanate terminated prepolymers (free isocyanates) matched with an amine curative, producing a highly flexible but tough polyurethane/polyurea matrix. Both coatings meet the minimum 180 minutes of erosion resistance, however, these systems fail to meet current needs in terms of VOCs, free isocyanates, and EHS concerns.

Based on the high solids content necessary to achieve the thickness, build, and durability to protect against rain erosion, such coatings contain high loadings of VOCs and HAPs constituents and both products contain high levels of free isocyanates. For example, CAAP produces rain erosion polyurethane coatings that meet performance requirements of both MIL-PRF-85322C

and SAE AMS-C-83231A, although the systems typically contain ~40wt% Xylene, 13wt% methylisobutylketone (MIBK), and various percentages of isocyanate compounds. Urethane or urea-based coatings have been formulated for lower VOC content and reduced HAPs but have not maintained the same level of rain erosion protection or the ability to eliminate the need for hazardous free isocyanate incorporation. Currently, no coatings are qualified to SAE AMS-C-83231A that can simultaneously meet the VOC requirements of MIL-PRF-85322C, contain no HAPs or free isocyanates, and meet the rain erosion requirements of SAE AMS-C-83231A.

### 3.2 GC Resin Chemistry

Two-component coating systems are coatings whose formulations contain mutually reactive functional groups that are mixed prior to application. These coatings are generally fast reacting thermosetting systems that result in films having excellent performance properties. The most common high performance two-component coatings are epoxy systems and isocyanate based polyurethane systems.<sup>9</sup> Glycidyl carbamate (GC) functional resins are a class of novel high performance non-isocyanate polyurethane (NIPU) resins. The GC reactive group consists of an epoxy adjacent to a carbamate (urethane) group (Figure 1). Reaction with an amine occurs via the epoxy group.



**Figure 1. Schematic of glycidyl carbamate resin functionality**

Luna has been conducting research on resins containing the GC reactive group for over a decade. This group has the functionality of an epoxy resin and provides the performance of a polyurethane coating without exposing the end-user (applicator) to isocyanates, as illustrated in Figure 1. Synthetic routes to produce GC functional oligomers have been developed by Luna and others including North Dakota State University (NDSU) over the past decade.<sup>10</sup> Results have demonstrated that the multifunctional GC resins with amine curing agents yield crosslinked polymers that exhibit excellent combinations of hardness, flexibility, and adhesion.<sup>11</sup> Kinetic experiments have also shown that the GC epoxy group is more reactive than a conventional glycidyl ether epoxy, resulting in fast cure times and a reduced time to topcoat.<sup>12</sup>

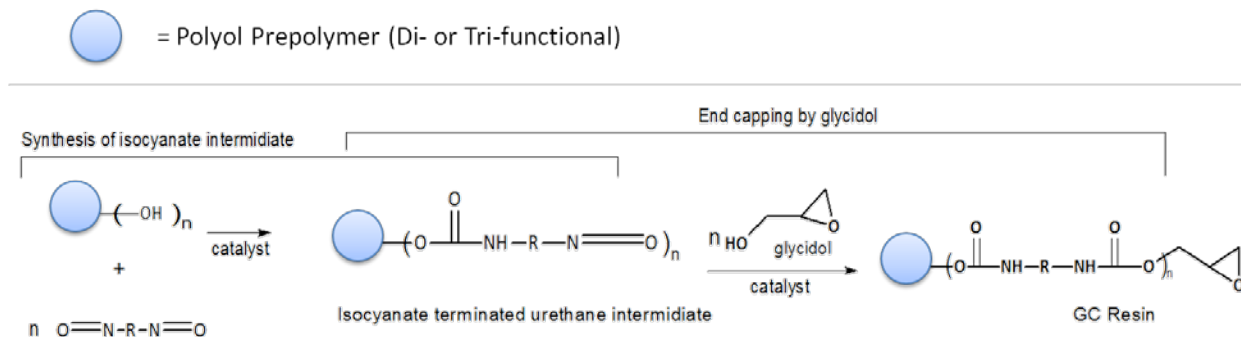
Coatings built on GC functional resins have a number of important features such as flexibility, cure speed, pot life, chemical resistance, and adhesion that make them excellent candidates for the preparation of highly flexible, low-VOC coatings systems. The distinctive advantage of the GC resin is that it is a hybrid resin system that blends the reactivity of epoxy systems with the properties of polyurethanes, without the hazards of free isocyanates. The polyurethane forms the flexible segment of the resin while the epoxy system provides the hard segments. Luna's system is tailorable to provide increased amounts of flexibility and/or hardness by modifying the GC resin chemical composition and the crosslink density of the finished coating.

The flexibility of GC coatings is highly dependent on the crosslink density. Polymers featuring lower crosslink density are expected to be more ductile. However, the drawback to increased ductility is decreased adhesion, solvent resistance, barrier properties (water, salt, oxygen), and hydrolytic stability. Crosslink density of the resin system can be reduced by decreasing functionality, increasing the MW, and adjusting the stoichiometry of the functional groups (epoxy to amine ratio). By optimizing the GC backbone's chemical structure and pairing the resin with a suitable amine curative, the resulting coating system can be tailored for specific applications. Luna previously developed a flexible non-chromate primer in the past utilizing the GC resin under two different Air Force programs (Air Force Phase I/II STTR, FA9550-09-C-

0150 and Phase I SBIR FA8650-16-M-5063). This primer was formulated to equal the performance of a chromated polysulfide primer under MIL-PRF-32239A. As such, it was developed to reach an elongation of 60% by GE reverse impact testing while maintaining flexibility at low temperatures. A major focus of the present effort was to build on Luna's previous work to make GC formulation modifications that increase flexibility, adhesion, toughness, and mechanical strength, eliminate free isocyanates and HAPs, reduce VOC levels further, and increase properties for increased rain erosion performance.

### 3.3 GC Resin Synthesis

The synthesis of the glycidyl carbamate functional group (Figure 1) by the reaction of an isocyanate functional compound and glycidol is well documented in the literature.<sup>10-13</sup> The general structure of Luna's GC resins consists of an epoxy functionalized polyurethane synthesized from a diisocyanate and a tri- or di-functional (linear) polyol. The materials used in Luna's current GC resin efforts expand on resin materials that were co-developed through this program and a separate Air Force SBIR Phase I (FA8650-16-M-5063).<sup>3</sup> The precursor materials used in the synthesis of a typical GC resin include a hydroxy terminated polyol of varying molecular weight, structure, and functionality.<sup>10</sup> The isocyanates used in the functionalization of polyol hydroxy groups can consist of di-functional isocyanates such as methylene bis-cyclohexylisocyanate (HMDI or hydrogenated MDI), isophorone diisocyanate (IDPI), methylene bis(4-phenyl isocyanate) (MDI), toluene diisocyanate (TDI), and hexamethylene diisocyanate (HDI). The epoxy end capping of the polyol-isocyanate structure is performed with the use of glycidol (hydroxy terminated epoxy). Figure 2 demonstrates the general route for synthesizing GC resins. After assembly of the reaction vessel and charging of the initial polyol reactant, the round bottom and contents are heated to the appropriate reaction temperature and molecular sieve dried methyl propyl ketone (MPK) or tertiary butyl acetate (TBAC, VOC exempt) are added under heavy nitrogen purge. Next, the diisocyanate is added with the addition being controlled so that the reaction did not go above the gelling point of the reaction materials. Once the reactor temperature is maintained, a commercially available metal catalyst is added and the temperature is once again controlled. The reactor contents are held at temperature for a minimum of 1 hour for the polyol-isocyanate reaction to come to completion. Titrations are performed on the contents to ensure complete functionalization of the polyol and minimization of free isocyanates. The structure of the intermediate resin is verified through Fourier transform infrared spectroscopy (FTIR). The result of this initial reaction is an isocyanate end capped polyol.



**Figure 2. Example GC resin synthesis route**

At the end of the isocyanate/polyol reaction, the excess isocyanate end groups are capped with an epoxy functionality using glycidol. Based on the titration determined isocyanate concentration, a slight excess of glycidol is added to the reactor with the temperature being maintained below 70 °C. After 30 minutes, the contents of the reaction vessel are analyzed through FTIR to see if the isocyanate peak is disappearing (reaction of the isocyanate and glycidol). If no change is apparent, additional catalyst is added. The reaction is allowed to proceed until the isocyanate peak has completely disappeared (verified through FTIR). The potential for free isocyanates is mitigated through small additions of methanol, ethanol, or isopropyl alcohol (IPA), which results in negligible isocyanate content.

The synthesis product is a high solids (>75 %), isocyanate free, GC resin. This procedure was applied to all of Luna's GC resins with modifications based on the precursor (equivalent weight of hydroxyl groups) or the diisocyanate.

### ***3.4 Luna's Rain Erosion Coating Formulations***

Luna's ultimate goal in this limited-scope program was to demonstrate coating performance relative to MIL-PRF-32239 and SAE AMS-C-83231A using the GC chemistry and simultaneously reducing VOCs, HAPs, and isocyanates. As such, careful consideration was given to the solvent package used in final formulations for spray application. Luna relied on the use of non-HAPs, VOC exempt solvents and minimal amounts of VOC contributing solvents to achieve the necessary formulation viscosity and produce a low-VOC formulation. The solvent package was carefully chosen to meet a 4-hour dry time while also minimizing the amount of non-VOC exempt solvents necessary for spray application. The solvent package of choice for formulating rain erosion coatings was tailored for proper film formation during spray application and curing/drying. Throughout this program, the solvent package was a combination of VOC exempt solvents and minimal loadings of the non-HAPS solvent MPK. Coatings buildup was achieved through consecutive application of 1-2 mil thick coatings over the course of 3-4 hours. All coatings developed were capable of dry to touch in 4 hours at a thickness of 10-12 mil.

Additional additives, including a variety of organic and inorganic fillers, thixotropics, and adhesion promoters, were added to formulations to increase the rheological properties and adhesion to common substrates as well as overall coating impact resistance, strength, and toughness. While the GC resins were synthesized in either MPK or TBAC, the solids content in these resins is high enough (greater than 75%) that their presence does not significantly influence the VOC content of the final coating systems. Additionally, the amine curatives used for curing/crosslinking were carefully selected to be of the high solids content variation in order to maintain a low VOC and non-HAPs formulation. The GC coating chemistry assessed in final program testing showed promise in reducing VOCs, HAPs, and isocyanates in a non-urethane chemistry, but solidified the fact that more optimization work is necessary to supplant current high VOC and isocyanate containing COTS systems and transition to rain erosion resistant GC coatings.

## 4.0 Materials and Methods

Substrates used for testing were predominantly aluminum alloys (AA) and fabricated glass fiber reinforced composites airfoils supplied by UDRI. Unless otherwise noted, substrates used for GE reverse impact testing and low temperature mandrel bend flexibility were bare AA2024-O at either 0.032” or 0.020” thickness. Substrates used for dry and wet tape adhesion testing were bare AA2024-T3 at 0.032” thickness. Substrates used for ultrasonic cavitation testing were standard AA2024-T3 (1” x 1”) coupons at 0.25”. For all GC resin formulations, the commercial pretreatment solution, PreKote, was acquired from Pantheon and applied following the manufacturer’s instructions. Rain erosion topcoats were coated onto substrates within two hours of the pretreatment application and cured under ambient conditions for 7 days. COTS rain systems were coated according to the manufacturer’s instructions using supplied pretreatments, primers, catalysts, accelerators and topcoats. All final rain erosion topcoats were applied at thicknesses of 10-12 mil before testing on the UDRI/AFRL rain erosion test apparatus, with the COTS rain erosion coating being applied at 10-12 mil over a 1-2 mil primer (total 12-14 mil coating system).

Materials for GC resin synthesis were acquired from various chemical suppliers. Several characterization tests were carried out on the GC resins after they were synthesized. These tests determined the resins solids percent, epoxy equivalent weight, and residual isocyanate content by FTIR using a Thermo Nicolet IR model 6700 in air on a Germanium plate attenuated total reflectance (ATR) accessory. Weight percent solids were determined by ASTM D2369. Epoxy equivalent weight was determined by titration following ASTM D1652.

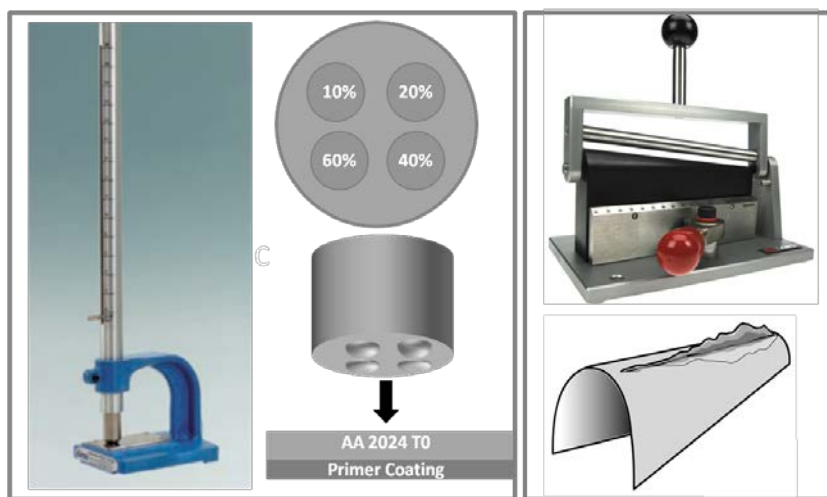
### 4.1 *Impact and Flexibility Testing*

Materials used for test panels conformed to standard military specifications for high solids primers and topcoats. A majority of the test panels used for flexibility testing, unless otherwise stated, were AA2024-O and were in accordance with SAE AMS-C-83231A and MIL-PRF-32239A. All panels utilizing Luna’s GC resins were pretreated with the non-chromate pretreatment system Prekote (Pantheon) prior to coating application. PreKote application was used in place of a traditional Alodine (hex- or tri-chrome) pretreatment as it is a fast and reliable pretreatment process and provides excellent coating adhesion, improved flexibility, and corrosion protection for a variety of substrates, including laminate and metallic substrates. PreKote has been used extensively at Luna as a non-chromate pretreatment alternative and has been highly recommended by Air Force coatings experts as a suitable replacement for contemporary technologies. Luna has past experience with the Prekote pretreatment and used it in combination with the developed GC topcoats. A standard wash primer was used for testing the COTS rain erosion product in place of the Prekote pretreatment (following technical specifications) and was supplied by the manufacturer (Aeroglaze 9947). The wash primer was used in place of a traditional conversion coating pretreatment (e.g. Alodine) at the recommendation of the manufacturer and has application to both laminate (composite) and metallic substrates.

GE reverse impact testing (Figure 3) was performed under ambient conditions on pretreated (or primed) AA2024-O coupons at 0.032” or 0.020” thickness. Panels were coated with relevant GC or COTS rain erosion coatings, placed on a rubber mat coated side down and impacted with a GE Universal impact tester from a height such that the diameter of the impact tester is imprinted onto

the backside of the panel. Shortly after striking, the impact sites were tested for cracking or pinholes down to the substrate with a holiday detector. Holiday detection was completed on coatings impacted at 10%, 20%, 40%, and 60% elongation. Coatings that do not exhibit pinholes at or above 40% meet the flexibility requirements of MIL-PRF-32239A.

Low temperature mandrel bend flexibility (Figure 3) was also performed on pretreated (or primed) 0.020" thick AA2024-O panels. Panels were coated with relevant GC or COTS rain erosion coatings and after a 7 day cure, the panels were placed in a freezer cooled to -54 °C with sufficient time to reach steady-state. Upon opening the freezer, coated surfaces were observed for cracking or any other defects. The flexibility was then tested on a conical mandrel bend apparatus cooled to -54 °C following ASTM D522 using a minimum ½" mandrel diameter. Any cracking, flaking or loss of adhesion at the 1" mandrel diameter constituted failure.



**Figure 3. GE reverse impact testing (left) and conical mandrel bend testing (right)**

#### **4.2 Adhesion Testing**

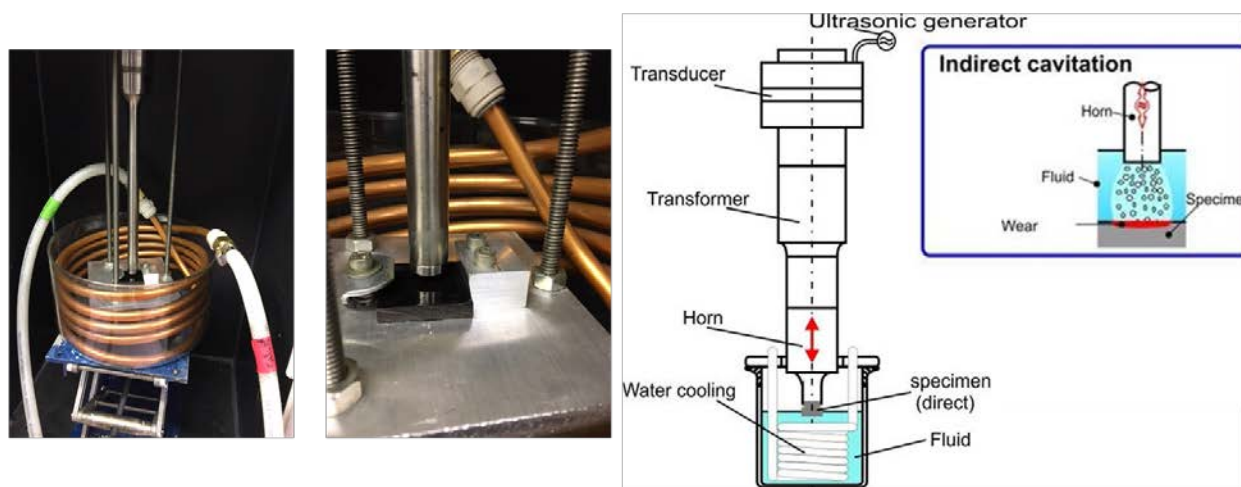
Dry adhesion testing was performed under ambient conditions on pretreated (or primed) AA2024-O at 0.032" thickness. Panels were coated with relevant GC or COTS rain erosion coatings and crosshatch adhesion was performed using a Gardco Paint Adhesion kit following ASTM D3359, wherein scribes were made with a carbide tip scribe tool with 11 horizontal cuts followed by 11 vertical making a grid pattern. The ASTM D3359 standard tape adhesion test was then performed. A rating of 4B and above meets the requirements of MIL-PRF-32239A.

Wet adhesion testing was performed under ambient conditions on pretreated (or primed) AA2024-O at 0.032" thickness. Panels were coated with relevant GC or COTS rain erosion coatings and after a 7 day cure, the panels were immersed in deionized (DI) water at room temperature for 24 hours. Upon removing the panel from the water, the coated surface was observed for any blistering, wrinkling, delamination, or other defects. Within three minutes of removing and dry wiping the panel, it was scribed in a similar manner to dry adhesion testing using a Gardco carbide scribe tool, after which the ASTM D3359 tape test was performed. A rating of 4B and above meets the adhesion requirements of MIL-PRF-32239A.



### 4.3 Ultrasonic Cavitation Testing

As a means of screening coating erosion resistance prior to full-scale rain erosion testing at UDRI, Luna developed a new test method using ultrasonic cavitation (vibratory apparatus) to simulate rain erosion (Figure 4). This test method employed a modified version of ASTM G32, *Standard Test Method for Cavitation Erosion Using Vibratory Apparatus*, and consisted of a horn sonicator that sits directly above coated coupons to create cavitation erosion. Per the ASTM G32 specification, the tip and coupon were immersed in a temperature controlled water bath and high-speed cavitation was directed from the sonicator tip to the coupon surface (in the form of a high-speed water/air stream). Luna initially evaluated the optimal conditions at which cavitation erosion occurs on a COTS coating system. For this effort, several coupons comprised of 1" x 1" aluminum were coated with the COTS coating. Coupons were submerged in the constant temperature water bath and the tip-to-coupon distance, power output of the sonicator, and time of sonication were varied. Through several rounds of testing, it was determined that a coating thickness of 2-3 mil, a maximum sonicator power output (10 W), a tip-to-sonicator distance of 0.5-2.0 mm, and a time between 10-30 minutes would simulate various levels of cavitation erosion on the COTS coating. Coatings tested under this method were evaluated for damage, and specifically, for degree of delamination, pitting, erosion, and total area of damage. Test coupons of both Luna's GC resins formulations and the COTS rain erosion coating system were evaluated under this method with the appropriate pretreatment. Coatings were applied at 2-3 mil thicknesses on the 1" x 1" aluminum coupons and allowed to cure for 7 days prior to testing. Damage to GC resin samples was directly compared to the COTS system and the best performing samples were down selected for full-scale rain erosion testing at UDRI.



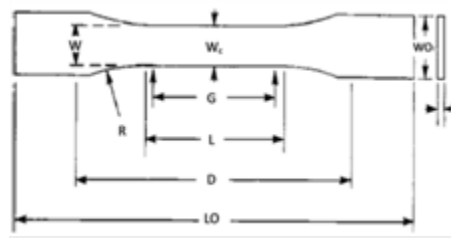
**Figure 4. Luna's ultrasonic cavitation test stand for running the modified ASTM G32 method.**

### 4.4 Mechanical Testing

Tensile testing was performed at room temperature on samples using an ADMET 2611 universal testing system. Samples of the GC topcoats and COTS rain erosion coating were prepared as free films (no substrate) and formed into dogbone coupons with a 1" gauge (Figure 5). Dogbone coupons were loaded into the ADMET grips and tested according to a modified version of ASTM D2370. Due to system strain rate limitations on the ADMET 2611, coupons were strained at a rate of 10 in/min (as opposed to 20 in/min in ASTM D2370) while the force and



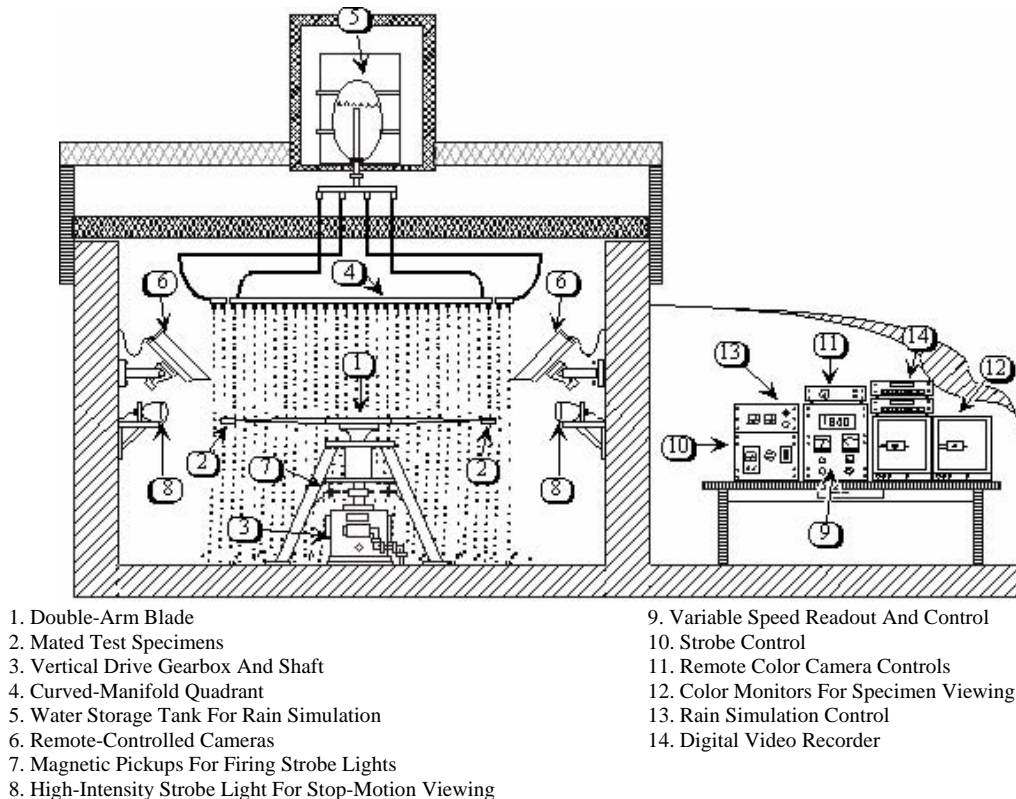
displacement were measured. Runs were performed in triplicate for each material type. Sample UTS and elongation at failure (break) was recorded and compared to the results of the COTS rain erosion coating.



**Figure 5. Example dogbone coupon prepared for free-film tensile testing of GC and COTS coatings.**

#### **4.5 Rain Erosion Testing**

After passing the appropriate performance metrics in flexibility, impact resistance, adhesion, and ultrasonic cavitation testing, down selected coating systems were evaluated for rain erosion performance. As rain erosion testing is the ultimate performance metric under the effort, Luna conducted rain erosion testing on AFRL's specialized test rig in accordance with SAE AMS-C-83231A requirements. The AFRL Rain Erosion Test Apparatus is the preeminent test method for proper coating assessment and is capable of attaining constant velocities between 100 and 900 miles per hour (Figure 6).



**Figure 6. AFRL Rain Erosion Test Apparatus**

Due to the high cost of testing at UDRI and the requirement that topcoats provide the majority of resistance to long-term rain erosion, Luna down selected only the best topcoat formulations for application to surrogate radome or airfoil substrates for testing. Glass fiber reinforced composite airfoils, materials typically used in traditional microwave transmissive radome applications, were purchased from UDRI for this effort. Coupons were coated with appropriate pretreatments prior to application of Luna's best performing GC resin topcoats or the qualified COTS product. The COTS rain erosion product was applied using the full coating package including pretreatment, wash primer, and topcoat (no anti-static coating). Coatings were spray applied via multiple coats to achieve a total thicknesses of 12-14 mil and allowed to cure at room temperature over the course of 7 days. The coated airfoils were then evaluated for defects, and only those that resulted in pristine coatings were tested at UDRI.

During testing, coated substrates were attached to the tip of a propeller blade that was rotated horizontally at a specific velocity through simulated 1-inch per hour rainfall. Raindrop conditions (2 mm diameter droplets) had randomly distributed impacts across the coating surface. The SAE AMS-C-83231A specification requires a propeller blade speed of 500 MPH and no erosion on a 12-14 mil thick coating after a minimum of 150 minutes under simulated rain conditions (primary goal of SAE AMS-C-83231A is survival after 180 minutes). All topcoat systems, including the COTS rain erosion coating, were run in duplicate.

The test duration can be designated at set increments, however, the test is typically terminated at the operator's discretion when erosion initiates. Damage is evidenced by coating loss or adhesion failure (Figure 7). Observed coupon descriptions were recorded as the test progressed, such as pitting, cratering, cracking, material loss or fracture, and delamination. Evaluations were reported as a function of time and coating failures in direct proximity to the specimen holder areas (<1 mm from the airfoil edge) were assumed to be attributed to the holder (anomalies).

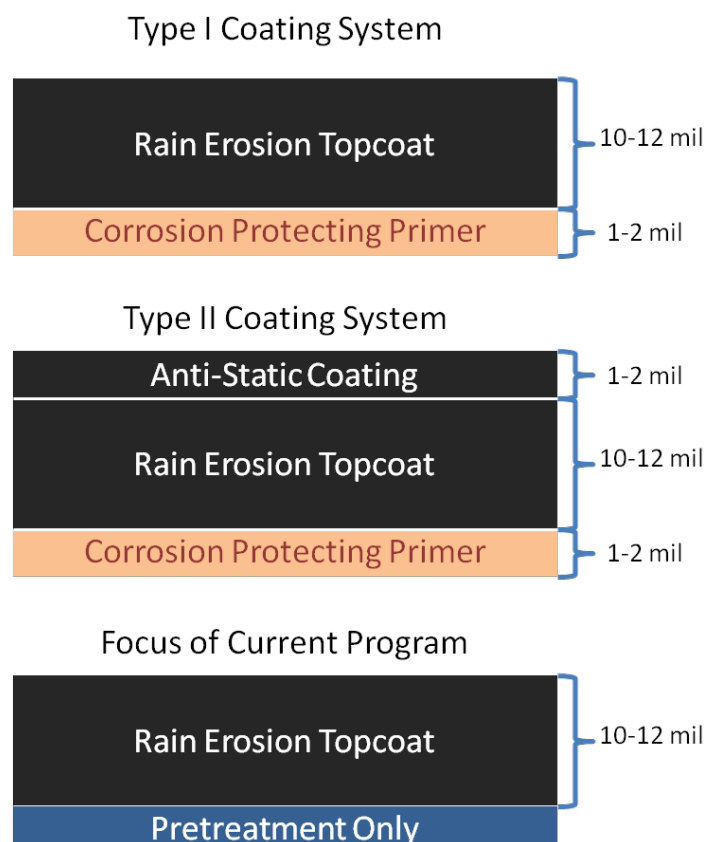


**Figure 7. Representative image of erosion initiation of a coated airfoil coupon on the AFRL Rain Erosion Test Apparatus**

## 5.0 Results and Discussion

Progress on the limited scope program was enabled by the completion of several individual tasks that culminated in characterization of multiple GC rain erosion coating variants. Primary focus of the base project was placed on developing an SAE AMS-C-83231A Qualified Class A, Type I coating system (i.e. without antistatic qualities) with specific focus on topcoat variants only. Flexible GC primers, developed under Luna's previous Air Force Phase I SBIR (FA8650-16-M-5063), will form the basis of the primer coating in continued development efforts. Under the prior Air Force effort, Luna developed a non-chromate corrosion inhibiting primer, based on the GC resin chemistry, which provided increased flexibility, impact strength, and adhesion as well as demonstrated corrosion protection in ASTM B117 salt fog testing. Rain erosion evaluation during this program was focused on the GC topcoat formulations (Figure 8). Once the efficacy of a topcoat only Type I system has been suitably demonstrated, Luna will begin development of a primer plus topcoat configuration as well as a Type II antistatic system in the next program funding stage. This system will include a 1-2 mil antistatic coating material that will overlay the rain erosion topcoat.

Luna's ultimate goal in the limited scope project was to increase flexibility, impact resistance, adhesion and erosion resistance using the unique GC hybrid resin chemistry. Luna placed an emphasis on coating systems for aircraft leading edges and radomes (10-12 mil topcoat). The following sections provide a detailed description of the accomplishments made throughout each program task.



**Figure 8. SAE AMS-C-83231A Qualified Class A, Type I and Type II coating systems and Luna's coating configuration during this effort.**

### **5.1 Task 1 – Coating Design**

The objective of this task was to review and confirm the performance requirements for rain erosion protective coatings and to formulate a variety of GC-based topcoats. During the kickoff meeting, Luna detailed the specific requirements and respective test methods that would be used to characterize and compare GC coatings to conventional rain erosion systems. Performance requirements and test methodologies were continuously reviewed throughout the program with an emphasis on meeting several key requirements in SAE AMS-C-83231A and MIL-PRF-32239A and matching or improving on the material and performance characteristics of commercial rain erosion systems. Properties of interest included low temperature flexibility, impact resistance, wet and dry adhesion, mechanical strength, and rain erosion resistance.

Luna's previous GC primer formulations, developed under Air Force SBIR Phase I (FA8650-16-M-5063), focused on adhesion, flexibility and corrosion resistance. Under this task, topcoat variants were developed with a focus on flexibility, impact resistance, adhesion, UTS, elongation at break, and rain erosion resistance. Luna reviewed existing resin formulations from past programs to make modifications to increase inherent flexibility and reduce resin viscosity to limit the need for additional VOC contributing solvents. The general structure of the GC resin consisted of a polyurethane synthesized from an isocyanate and a tri- or di-functional (linear) polyol. At the end of the isocyanate/polyol reaction, excess isocyanate end groups were capped with epoxy functionality with negligible isocyanate content remaining in the formulation (confirmed by FTIR spectroscopy).

Formulated topcoats were produced to be low VOC, non-HAPs, and isocyanate free with the goal of maintaining all other properties for performance against SAE AMS-C-83231A and MIL-PRF-32239. Prior to this program, Luna's most recent GC coating formulation was VOC compliant (<340 g/L) according to MIL-PRF-32239A, however, Luna targeted <100 g/L over the course of this program. Example exempt solvents that were investigated in this program included Oxsol-100™ (parachlorobenzotrifluoride), acetone, tertiary butyl acetate (TBAC), and methyl acetate. Such solvents were utilized in both the Part A (GC) and Part B (amine curative) sides of each coating variant to displace the need for VOC solvents. These solvents also allowed for control of the evaporation rate of the solvent package to allow for strong film development coupled with a rapid flash-off time. The resin-solvent formulations developed under this task were designed for rapid film build up, fast recoat time, and a reduced complete cure time compared to incumbent rain erosion coatings.

Enhancing the toughness of the topcoat layer, a priority in this program, was accomplished through the introduction of additional organic and inorganic additives to improve wear resistance, mechanical strength, and overall durability. The resin chemistry was adjusted to increase hydrogen bonding, improve hydrolytic stability, and optimize the GC resin for an ideal functionality, structure, and molecular weight (MW).

#### **5.1.1 Rain Erosion Primer and Topcoat Formulation**

In past primer development efforts, the A side was cured with an amine or polyamide curative. When fully-formulated with appropriate non-chromate corrosion inhibitors, functional additives, and solvents, primers passed nearly all metrics when tested against MIL-PRF-32239A. The performance metric the GC primers failed in some cases was resistance to extended water immersion or ASTM B117 salt fog testing (i.e. some of the panels exposed to water for extended times blistered, but not all). There are several ways to improve the moisture resistance of GC

coating systems, which Luna has demonstrated on related projects. These include i) incorporation of hydrolytically stable polyol precursors, ii) incorporation of urea hard segments for improved water barrier properties via the urea bond as well as increased toughness for rain erosion resistance, and iii) incorporation of an amine curative with enhanced hydrolytic stability and excellent water barrier properties. Due to the flexibility of the GC chemistry, each of these formulation changes can be easily utilized within the coating to assess improved performance in both durability and water resistance. Several of these additions were performed under this approach and resins were thoroughly assessed for water resistance (wet adhesion testing) prior to full formulation with a relevant additive package.

Luna synthesized one GC resin during this limited scope program and purchased three additional GC resins prepared by Dean Webster at NDSU (Table 1). The three GC resins from NDSU were variants of previous evaluated resins with slight modifications to the polyol backbone and isocyanate functionality (prior to epoxy functionalization). All four resins (Table 1) were free of isocyanates and contained high solids content (>75%) with minimal loadings of the residual solvents. Each resin was characterized for solids content and epoxy equivalent weight prior to formulating.

**Table 1. Luna and NDSU GC resins**

GC Resin	Prepolymer	Epoxy Equivalent Weight (g/mol)	Solids Content (%)
GC 1	Trifunctional Polyol Isocyanate 1 Glycidol	946	80
GC 2	Linear Polyol Isocyanate 1 Glycidol	591	88
GC 3	Linear Polyol Isocyanate 2 Glycidol	756	80
GC 4	Linear Polyol Isocyanate 1 Glycidol	1046	80

Luna focused heavily on matching the GC resin (part A) side of the chemistry with appropriate amine/amide curatives to enable highly flexible, yet tough, polymer coatings. Luna assessed a variety of COTS amine and polyamide curatives that have been shown to enhance the flexibility of traditional epoxies and increase hydrolytic stability and impact resistance. Eight different COTS curative systems were procured from several vendors, including Air Products, Hexion, Gabriel (former BASF product line), and Cardolite. After extensive testing, two polyamides and one amine were identified as the most promising curatives for formulating hydrolytically stable, flexible and impact resistant coatings with the Luna and NDSU GC resins. Of these three epoxy curatives, Luna worked heavily with a single amine curative with excellent hydrolytic stability and water resistance.

Luna's ultimate goal in the design of the topcoat was increased flexibility and impact resistance by removing unnecessary additives and by incorporating wear resistant materials for excellent toughness and impact strength. The desired formulation (GC resin, amine curative, additive package) was a topcoat that equals or surpasses the performance of commercial rain erosion

coating systems. Topcoats were formulated with various color additives, such as carbon black (CB) and titanium dioxide (TiO<sub>2</sub>) for proper color pigmentation and DoD use. Initially, a transmissive white (TiO<sub>2</sub>) variant was targeted, but other colors were also explored including black coatings using CB. Balanced filler loading levels and proper interfacial compatibility were required in order to maximize rain erosion performance, film strength, and flexibility, and to prevent issues with microwave radar transmission through the use of non-conductive, dielectric additives. These additives included toughening agents, such as glass microbubbles, ceramic microspheres, aerogel particles and rubber additives, as well as strengthening additives such as non-conductive CB powders and silicon carbide (SiC) fibers. Additives were expected to have a significant effect on the durability of the GC coatings and overall rain erosion performance.

Careful consideration was also given to the rain erosion topcoat solvent package during this effort. Under SAE AMS-C-83231A, the rain erosion topcoat layer must be applied at a 10-12 mil coating thickness, leading to significant VOC contribution in COTS rain erosion coating systems. COTS coatings have specified interval windows between spray applications (layering or build up that ranges from 10 to 30 minutes between coats) and require 4 or more hours to reach a 10-12 mil thickness and 7 days for full cure. Long application times in COTS coatings is a direct result of the high solvent loading package and very thin coating build up (<1 mil per coat). To reduce applicator coating time and coating build rate, Luna designed rain erosion topcoats to be applied at 1-2 mil thickness in under 4 hours. Luna focused on the use of specific non-HAPs and VOC exempt solvent packages for this effort. These solvent systems aimed to achieve thicker GC layer build up during spraying, rapid flash off and cure times between layers, and the necessary formulation viscosity to maintain optimized spray conditions. The solvent package was chosen to maintain the 4-hour dry time of the final 10-12 mil coating while also minimizing the amount of non-VOC exempt solvents necessary for spray application. The solvent package of choice for topcoat formulation was based on a combination of several VOC-exempt solvents, including acetone, TBAC, and Oxsol™, and low loadings of VOC contributing solvents such as MPK (in addition to the VOC contributing solvents present in the GC resin, or part A, side of the formulation). All topcoats developed throughout this program contained ~150 g/L VOC content and were capable of dry to touch in 4 hours and a full cure within 7 days.

#### *5.1.2 Coating Synthesis, Mixing, and Documentation*

Full coating formulations were prepared using standard mixing equipment, such as pneumatic or electric mixers with high-shear blades. Standard coating procedures were employed throughout the development process so that eventual transition to a toll manufacturer may be easily facilitated if desired later in a follow-on project. Luna also developed initial draft SDS documentation to satisfy EHS requirements. The GC component exhibits very low EHS hazards, but as it is a new chemical component, Luna will ultimately register the chemistry through the appropriate EPA channels. Luna has experience generating such documentation, successfully TSCA registering a new urethane-based aircraft product in 2014 for DoD use. Appropriate EPA and TSCA registration planning early in a follow-on coating development effort will help facilitate transition at higher technology and manufacturing readiness levels.

### **5.2 Task 2 – Coating Performance Characterization**

The objective of this task was to evaluate the leading rain erosion topcoat formulations against key metrics in the SAE AMS-C-83231A and MIL-PRF-32239 specifications, with specific

emphasis placed on those stated as critical and desired performance properties in the appendix of the WPSO-16-02 solicitation (duplicated here in APPENDIX A). Properties of interest included flexibility, adhesion, impact resistance, and rain erosion resistance. All GC topcoat formulations were compared against the COTS rain erosion coating (referred to here as COTS RE). The following sections provide detailed results from coating formulation and characterization. Detailed results from Luna's GC primer development can be found in Luna's Air Force SBIR Phase I final report (AFRL-RX-WP-TR-2017-0013).<sup>14</sup>

#### *5.2.1 Luna's GC Rain Erosion Topcoat Performance*

The development of Luna's GC based rain erosion topcoat was based on preliminary data from GE reverse impact, low temperature flexibility, and adhesion testing of previously developed GC primers (AFRL-RX-WP-TR-2017-0013).<sup>14</sup> During this initial primer development, GC 1, GC 3 and GC 4 showed the highest range of flexibilities (impact and low temperature mandrel bend) and greatest adhesion with the use of a single amine curative. GC 2 demonstrated poor performance in both tests and was not evaluated further. To evaluate the suitability of these coatings as the rain erosion topcoat layer, Luna developed additional formulations free of corrosion inhibitors and other silicate additives. GC topcoats were formulated to contain no residual free-isocyanates or HAPs in the topcoat formulation. Careful consideration was given to the rain erosion topcoat solvent package during this effort so that coatings could be applied at up to 10-12 mil coating thickness. Luna designed the initial GC topcoat solvent package so that coatings could be applied within shorter periods of time and at thicker build rates. The developed GC topcoats contained ~150 g/L VOC content and could be applied at 1-2 mil thicknesses with complete 10-12 mil build up in less than 4 hours.

The initial goal in Luna's rain erosion topcoat development was retesting the impact, flexibility, and adhesion performance of the previously developed primer coating systems with the topcoat specific additive and solvent packages. In lieu of applying 10-12 mil coatings of each formulated topcoat, Luna chose to apply coatings at a 3 mil thickness for appropriate impact, flexibility, and adhesion testing. While coatings at 10-12 mil thickness provide details on the performance of the final rain erosion topcoat product, these thicknesses do not comply with the standard test methods set forth in MIL-PRF-32239A for the evaluation of flexible, impact resistant coatings.

Determining the impact resistance and flexibility of the GC rain erosion topcoats was critical in this effort as flexibility and impact resistance of the topcoat layer can be a sign of excellent rain erosion performance. Particular focus was given to GE reverse impact testing per ASTM D6905 to determine impact resistance, overall flexibility and adhesion. Table 2 shows the results of GE reverse impact testing on the COTS RE coating and GC 1, 3, and 4 topcoats with the selected amine curative, additional amine adhesion promoter, and minimal loadings of a CB color pigment. Coupons were tested in duplicate and all coatings were evaluated for cracking/pinholes immediately after impact. The COTS RE coating and all three GC topcoats provided excellent elongation up to 60%.



**Table 2. GE reverse impact testing of GC topcoats and COTS RE coating**

Resin	Run 1	Run 2
GC 1	60%	60%
GC 3	60%	60%
GC 4	60%	60%
COTS RE	60%	60%

To test flexibility, coupons were flexed over a conical mandrel according to ASTM D522 after a one hour -54 °C exposure (mandrel bend from 1" to ½"). Pinholes and cracking were assessed following flexing (Table 3). The COTS RE coating and Luna's GC 1 and GC 4 topcoat variants provided excellent flexibility under this test. Coatings were capable of a 1" mandrel bend with flexing as low as ½". GE reverse impact testing showed that the GC 1 and 4 also provided excellent impact resistance; however, the GC 3 (previously 60% elongation) showed poor low temperature flexibility (failure).

**Table 3. Low temperature mandrel bend testing of GC topcoats and COTS RE coating**

Resin	Run 1	Run 2
GC 1	½" (Pass)	½" (Pass)
GC 2	1" (Fail)	1" (Fail)
GC 3	½" (Pass)	½" (Pass)
GC 4	½" (Pass)	½" (Pass)
COTS RE	½" (Pass)	½" (Pass)

Dry and wet adhesion testing was performed in duplicate on AA2024 T3 panels with the COTS RE coating and GC topcoats. Wet adhesion panels were immersed in DI water for 24 hours prior to evaluation. Adhesion was evaluated by comparison in ASTM D3359. Table 4 shows the adhesion properties of the COTS RE coating and three GC topcoat variants. All GC topcoats provided excellent dry and wet adhesion (5B, passing MIL-PRF-32239A standards), however, the COTS coating system showed extensive wrinkling, delamination, and adhesion failure (0B).

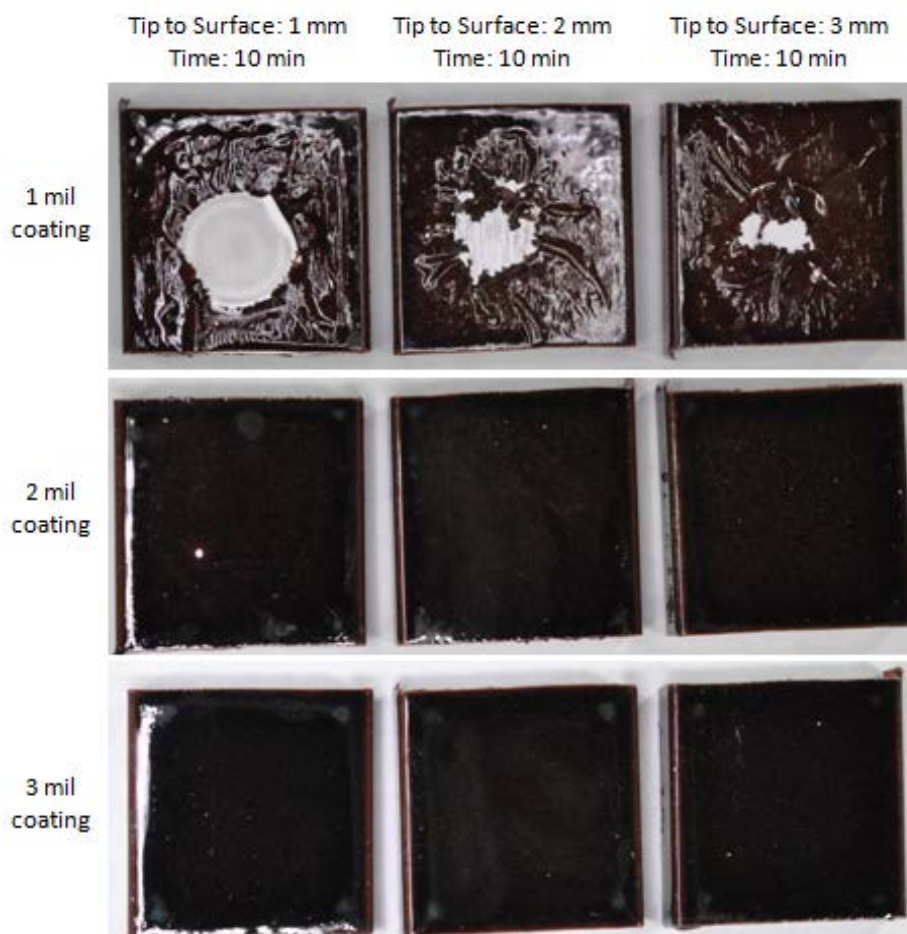
**Table 4. Dry and wet adhesion of GC topcoats and COTS RE coating**

Resin	Dry Adhesion		Wet Adhesion	
	Run 1	Run 2	Run 1	Run2
GC 1	5B	5B	5B	5B
GC 3	5B	5B	5B	5B
GC 4	5B	5B	5B	5B
COTS RE	5B	5B	0B	0B

After evaluating impact resistance, flexibility, and both dry and wet adhesion properties, the COTS RE coating and three GC topcoats were evaluated using Luna's in-house ultrasonic cavitation method. Coatings were applied to 1" x 1" AA2024 coupons, allowed to cure for 7



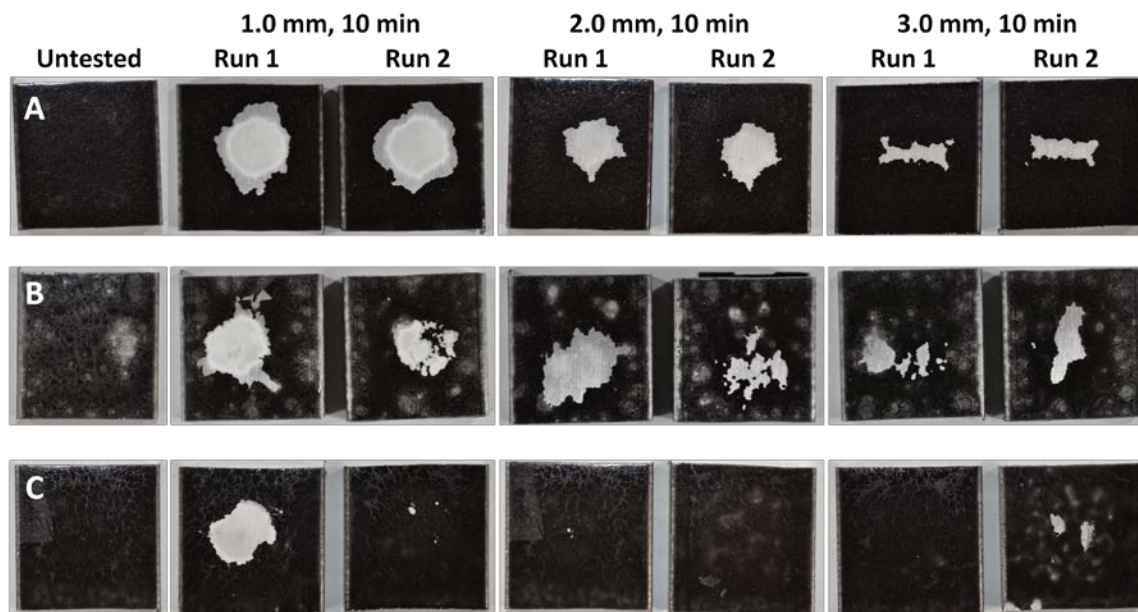
days, and immersed in a constant temperature bath for 10 minutes prior to sonication. Initial testing was performed on the COTS RE coating to determine the appropriate coating thickness for assessing formulation variants developed under this effort. The COTS coating was coated at 1- 3 mil thicknesses and evaluated at a tip-to-surface distance between 1-3 mm for a total of 10 minutes (at sonicator full power). Figure 9 shows the results of ultrasonic cavitation testing on the COTS rain erosion coating. At a 1 mil thickness, the COTS coating showed extreme wrinkling, delamination, and cavitation erosion. At thicknesses of 2 and 3 mil, the coating showed minimal erosion without visible delamination or wrinkling with the 3 mil coating showing no signs of degradation or pitting up to 20 minutes of cavitation testing.



**Figure 9. Ultrasonic cavitation testing of the COTS RE coating system at coating thicknesses of 1-3 mil**

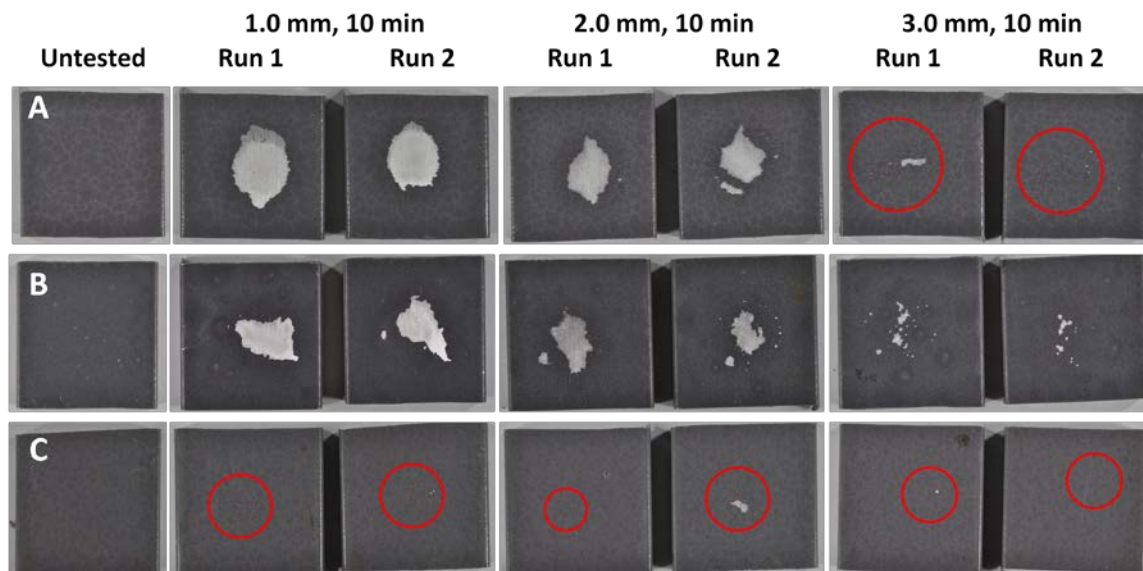
After evaluating the COTS RE coating system, it was determined that a coating thickness of 3 mil provided excellent resistance to cavitation erosion, pitting and coating delamination. As a comparison, GC topcoat variants were applied to AA2024 coupons at a 3 mil thickness and were evaluated at a tip-to-surface distance between 1-3 mm under identical conditions. Figure 10 shows the results of ultrasonic cavitation testing on the GC topcoats. These coatings showed no signs of wrinkling or delamination; however, all coatings at a tip-to-surface distance of 1 mm showed extreme pitting and cavitation erosion. At 2-3 mil thicknesses, the GC 1 and GC 3 topcoats showed similar cavitation erosion with the GC 3 having film formation issues during coating development (fish eyes and improper film formation). The GC 4 topcoat was the best

performing Luna system with minimal erosion at a 2-3 mm tip-to-surface distance but this coating also showed slight issues in coating film formation.



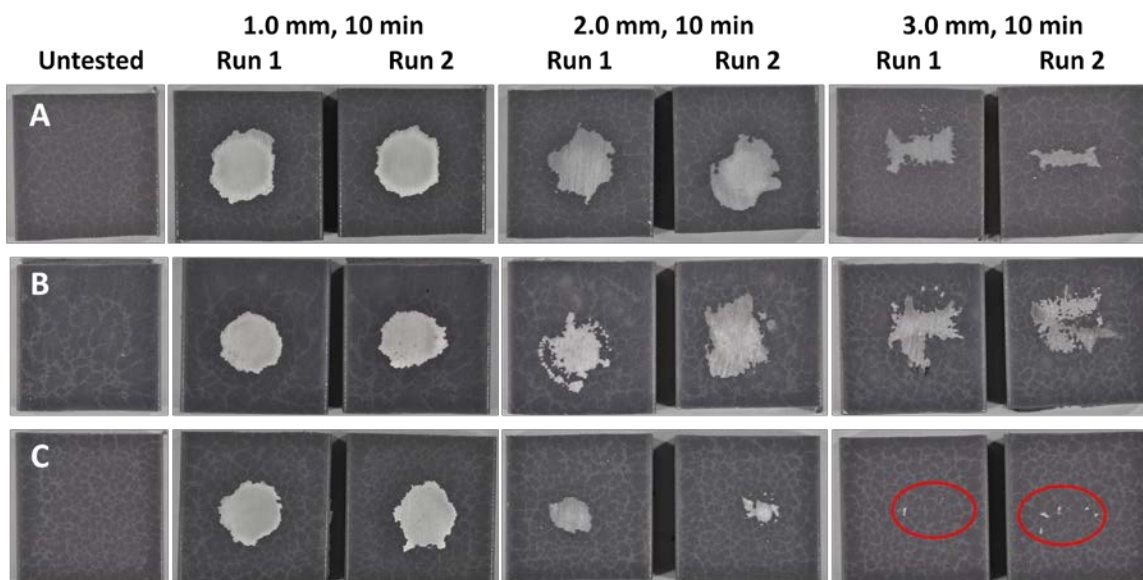
**Figure 10. Ultrasonic cavitation testing of Luna's GC 1 (A), 3 (B), and 4 (C) topcoats at a 3 mil coating thickness**

To improve the performance of the GC topcoat formulations, Luna investigated the use of an updated solvent package, a modified carbon black (CB) loading level, and the addition of various additives that could improve the wear resistance, impact resistance, and overall rain erosion durability. These additives included toughening agents, such as glass microbubbles, ceramic microspheres, aerogel particles and rubber additives, as well as wear resistant and strength improving additives such as silicon carbide (SiC) fibers. Luna initially investigated the addition of low loadings of zeeospheres, a semi-transparent, high-strength ceramic microsphere that has proven success in improving hardness and abrasion resistance in coating applications. Figure 11 shows the results of ultrasonic cavitation testing on the GC topcoats with low loadings of the zeeosphere additive. At a 3 mil thickness, the coatings showed signs of improvement in cavitation erosion performance, with the GC 1 and GC 3 topcoats having small improvements at tip-to-surface distances of 1, 2, and 3 mm and the GC 4 topcoat having the best performance at all distances. At distances of 1, 2, and 3 mm, the GC 4 showed minimal pitting, no coating delamination and limited cavitation erosion.



**Figure 11. Ultrasonic cavitation testing of Luna's GC 1 (A), 3 (B), and 4 (C) topcoats at a 3 mil coating thickness with a low loading of zeeospheres. Red circles indicate visible erosion and small amounts of coating pitting.**

Luna also investigated the addition of glass microbubbles, a glass ceramic additive that has been shown to increase coating stability under harsh wear and abrasion conditions. Figure 12 shows the results of ultrasonic cavitation testing on the GC topcoats with low loadings of glass microbubbles. Even at a 3 mil thickness, the GC coatings showed limited improvement in cavitation erosion performance, with the GC 1 and GC 3 topcoats having similar erosion compared to the additive free coatings. At a tip-to-surface distance of 3 mm, the GC 4 with a low loading of glass microbubbles exhibited modest improvement in cavitation erosion resistance.

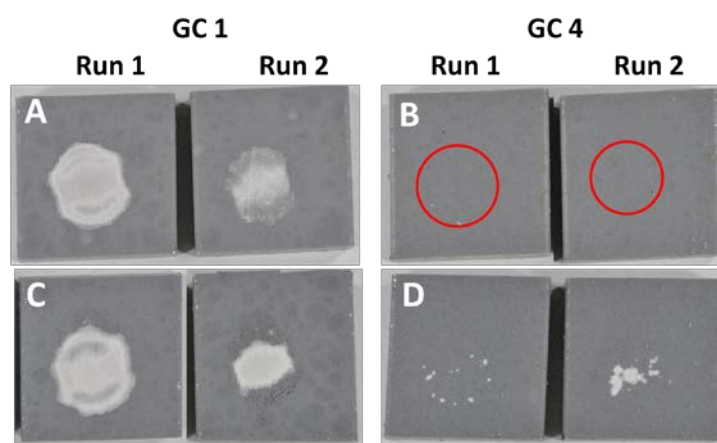


**Figure 12. Ultrasonic cavitation testing of Luna's GC 1 (A), 3 (B), and 4 (C) topcoats at a 3 mil coating thickness with a low loading of zeeospheres. Red circles indicate visible erosion and small amount of coating pitting.**

After testing initial topcoat formulations with zeeospheres and glass microbubbles, Luna reevaluated the impact resistance, low temperature flexibility, and dry/wet adhesion of the GC variants. Luna determined that the addition of both the zeeospheres and glass microbubbles had no effect on the GE reverse impact flexibility of the coating variants, with all formulations capable of 60% elongation. In low temperature flexibility and dry/wet adhesion testing, the GC 1 and GC 4 formulations were capable flexing over a 1" diameter mandrel without cracking or delamination and showed excellent adhesion, with 5B ratings in both dry adhesion testing and wet adhesion testing after 24 hour immersion in DI water. The GC 3 coating formulations with both the zeeospheres and glass microbubbles showed similar capabilities in GE reverse impact testing (60% elongation), but continued to show cracking and delamination in low temperature flexibility testing. While both the dry and wet adhesion performance of the GC 3 formulations were still ideal (5B rating), the continued low flexibility and inadequate film properties (fish eye) led to removal of GC 3 from future coating formulation efforts.

In an effort to continue improving the performance of the GC 1 and GC 4 topcoat formulations, Luna investigated the use of three additional additives. Topcoats were formulated with the addition of low loadings of (1) a low density ceramic based aerogel microparticle with improved impact resistance, (2) an amine terminated rubber additive with high flexibility and toughening capabilities, and (3) a silicon carbide (SC) fiber proven to increase the abrasion resistance and strength in various coating applications. Figure 13, Figure 14 and Figure 15 show the results of ultrasonic cavitation testing on the GC topcoats with low loadings aerogels, rubber additives, and SiC fibers. Coatings were evaluated at a tip-to-surface distance of 2 mm over 10 minutes.

Figure 13 shows the results of ultrasonic cavitation testing on the GC 1 and GC 4 topcoats with low loadings of the aerogel additive. At a 3 mil thickness, the GC 1 topcoat showed continued signs of cavitation erosion (1.5 and 3.0 wt % loadings). At similar loading levels, the GC 4 topcoat showed almost no pitting or coating delamination with excellent erosion resistance at a loading of 1.5 wt % and a slight performance drop at 3.0 wt %.

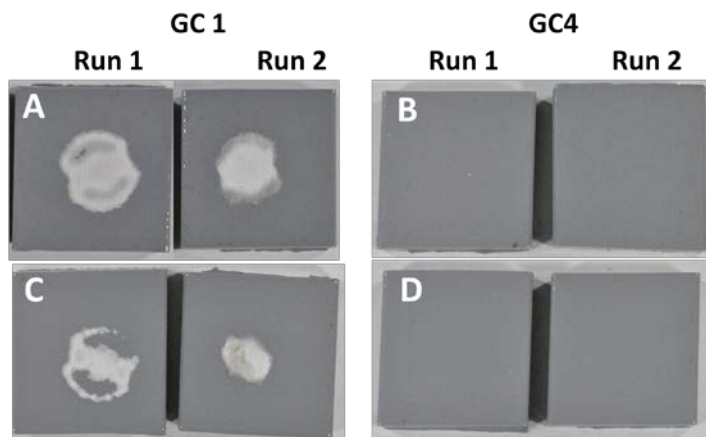


**Figure 13. Ultrasonic cavitation testing of Luna's GC 1 and GC 4 topcoats with the aerogel additive at a 3 mil coating thickness and tip-to-surface distance of 2 mm. Aerogels were incorporated at loading levels of 1.5 wt % (A,B) and 3.0 wt % (C,D). Red circles indicate visible erosion and small amount of coating pitting.**

Figure 14 shows the results of ultrasonic cavitation testing on the GC 1 and GC 4 topcoats with the amine terminated rubber additive. With low loadings of the amine terminated rubber additive, the GC 1 topcoat showed no improvement in cavitation erosion testing (3.0 and 6.0

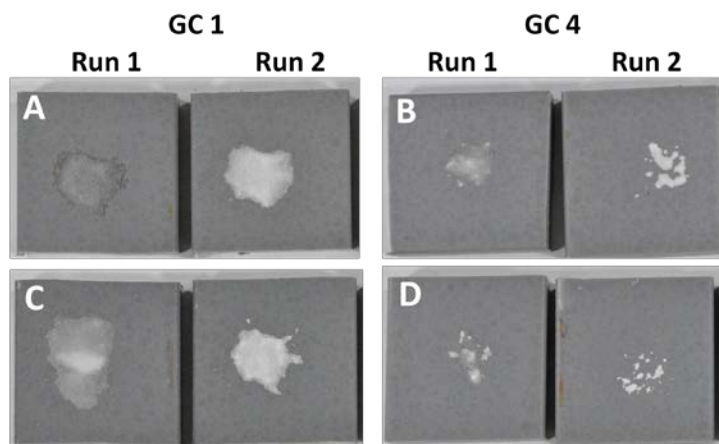


wt% loading). The GC 4 topcoat demonstrated improved resistance against pitting, delamination, and erosion and demonstrated similar performance to the COTS RE coating.



**Figure 14. Ultrasonic cavitation testing of Luna's GC 1 and GC 4 topcoats with the amine terminated rubber additive at a 3 mil coating thickness and tip-to-surface distance of 2 mm. Rubber additives were incorporated at loading levels of 3.0 wt % (A,B) and 6.0 wt % (C,D).**

Figure 15 show the results of ultrasonic cavitation testing on the GC topcoats with low loadings of the SiC fiber additive. GC 4 topcoats with SiC showed an improvement in preventing pitting, delamination, and erosion. Erosion still occurred during the 10 minute run time but with increased performance at a SiC loading level of 3 wt % and slight drop in performance at 6 wt %. With the addition of the SiC fibers, the GC 1 topcoat formulation showed only a slight improvement in erosion at loading levels of 3 and 6 wt %.



**Figure 15. Ultrasonic cavitation testing of Luna's GC 1 and GC 4 topcoats with the SiC fiber at a 3 mil coating thickness and tip-to-surface distance of 2 mm. SiC was incorporated at loading levels of 3.0 wt % (A,B) and 6.0 wt % (C,D).**

After evaluating the GC 1 and 4 topcoats with the previous additives, Luna reevaluated the impact resistance, low temperature flexibility, and dry/wet adhesion. The addition of the aerogels, rubber additives, and SiC fibers had no effect on the GE reverse impact resistance and adhesion of the coating variants, with all formulations capable of 60% elongation and 5B adhesion rating. In low temperature flexibility and dry/wet adhesion testing, the GC 4

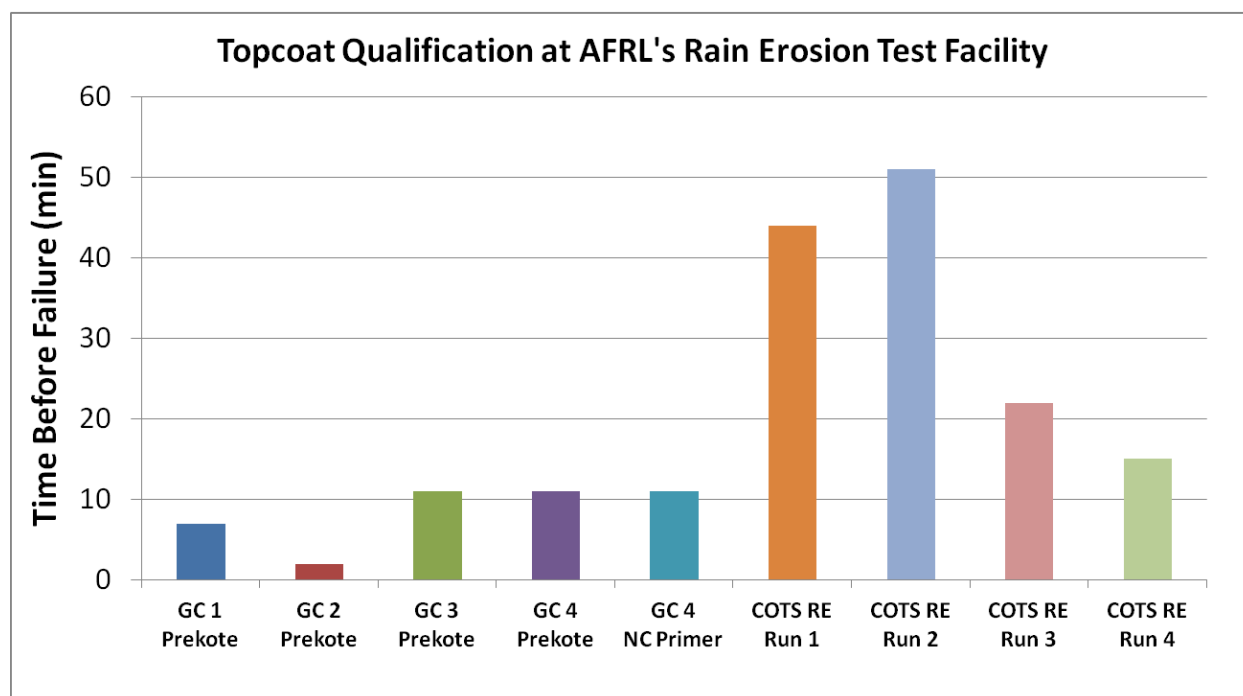
formulations were capable of being flexed over a 1” diameter mandrel without cracking or delamination and showed excellent adhesion. GC 1 with both the rubber additives and SiC fibers showed a decreased capability in low temperature flexibility testing and several coatings peeling and delaminating.

### ***5.3 Task 3 – Full Scale Rain Erosion Testing***

The objective of this task was to review the best performing GC rain erosion topcoats throughout the course of the program and evaluate their performance on the AFRL Rain Erosion Test Facility’s full-scale test rig. Six full days of rain erosion testing were originally scheduled at AFRL, however, during the course of the program it was found that more samples could be run per day of testing than originally planned. Luna evaluated GC rain erosion topcoats (PreKote pretreatment plus topcoat) and the COTS RE coating (primer plus topcoat) several times throughout the program. Three full days of testing at AFRL were used in the process of optimizing and evaluating Luna’s GC variants in an effort to increase the survival time under SAE AMS-C-83231A rain erosion conditions (500 mph, 1”/hour rain fall, 2 mm diameter water droplets). In all tests, GC variants were coated on fabricated glass fiber composite airfoils supplied by UDRI and all coatings were compared against the COTS rain erosion coating system, which has been shown to pass 150-180 minutes of rain erosion testing under SAE AMS-C-83231A conditions. GC formulations were coated at a thickness of 10-12 mil while the COTS RE coating was applied on top of a 1-2 mil primer at a thickness of 10-12 mil. The objective of this effort was to evaluate rain erosion performance and determine whether the properties provided by the GC resin chemistry showed promise for continued development.

#### ***5.3.1 Rain Erosion Demonstration at AFRL***

Luna conducted an initial day of testing early in the program that focused on testing additive free GC topcoat materials (GC 1, 3, and 4) at a coating thickness of 10-12 mil. These formulations were based on initial GC primer variants modified to have a decreased additives package (non-chromate corrosion inhibitors and other additives removed) as well as a slightly modified solvent package for improved coating build up and cure rate. Luna also evaluated several airfoil coupons of the COTS RE coating. The COTS product utilized a wash primer in place of the PreKote pretreatment and was coated at a total thickness of 12-14 mil. To determine whether pretreatments or primers have an effect on the rain erosion performance under SAE AMS-C-83231A testing, Luna prepared an additional GC 4 formulation sample with the use of a non-chromate corrosion inhibiting primer in place of the PreKote pretreatment (Deft/PPG 02GN084 non-chromate epoxy primer, 1-2 mil thickness). Figure 16 shows the results of Luna’s initial round of testing on the AFRL test rig under SAE AMS-C-83231A rain erosion conditions.

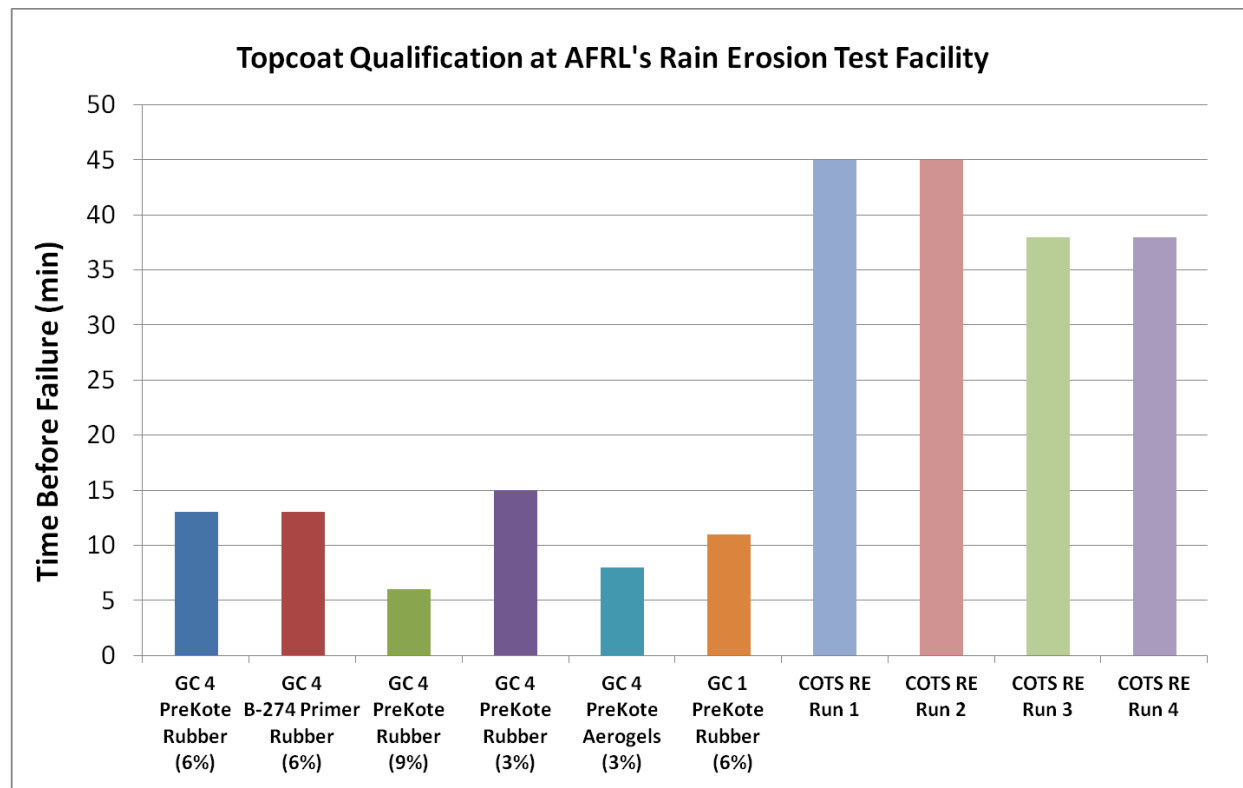


**Figure 16. Initial round of rain erosion testing at AFRL's Rain Erosion Test Facility. Testing was conducted on Luna's GC 1-4 topcoat variants with the PreKote pretreatment and an additional GC 4 topcoat with the Deft/PPG 02GN084 Non-chromate epoxy primer. Luna's topcoats were compared against the COTS RE coating.**

Under SAE AMS-C-83231A conditions, the COTS RE coating was capable of surviving 33 minutes of rain erosion on average, which is significantly lower than the manufacturer's specified rating of 150-180 minutes. The decreased performance in the COTS product was not anticipated, however, coatings were shown to have slight "popping" or blistering at the surface. This pre-existing condition was hypothesized to be the source of premature failure of the COTS coating system and was corrected for the final round of testing at AFRL through the acquisition of a fresh batch of the COTS rain erosion system (see Figure 19). Luna's GC topcoat variants showed decreased rain erosion resistance during testing on the AFRL test apparatus. The GC 3 and GC 4 variants averaged 11 minutes under SAE AMS-C-83231A conditions with both the GC 1 (9 minutes) and GC 2 (11 minutes) showing limited rain erosion resistance. No additional improvement was observed with the incorporation of the non-chromate primer (GC 4, 11 minute duration).

Luna conducted a second day of rain erosion testing prior to mechanical test evaluation on the base GC topcoat formulations (Figure 17). Testing focused on the best performing GC rain erosion topcoats from ultrasonic cavitation testing (Task 2). A majority of the formulations were based on the GC 4 topcoat with the addition of the amine terminated rubber additive (3-9 wt %) and the ceramic aerogel (3 wt %). The GC 4 topcoat variants showed only a modest improvement in rain erosion resistance during this round of testing, with no coating surpassing 15 minutes under SAE AMS-C-83231A conditions. The GC 4 with various loadings of the rubber additive previously showed improved cavitation erosion resistance, but were only capable of passing 15 minutes (3 wt%), 13 minutes (6 wt%) and 6 minutes (9 wt%) of rain erosion testing, indicating a drop in performance with increased loading of the rubber additive but

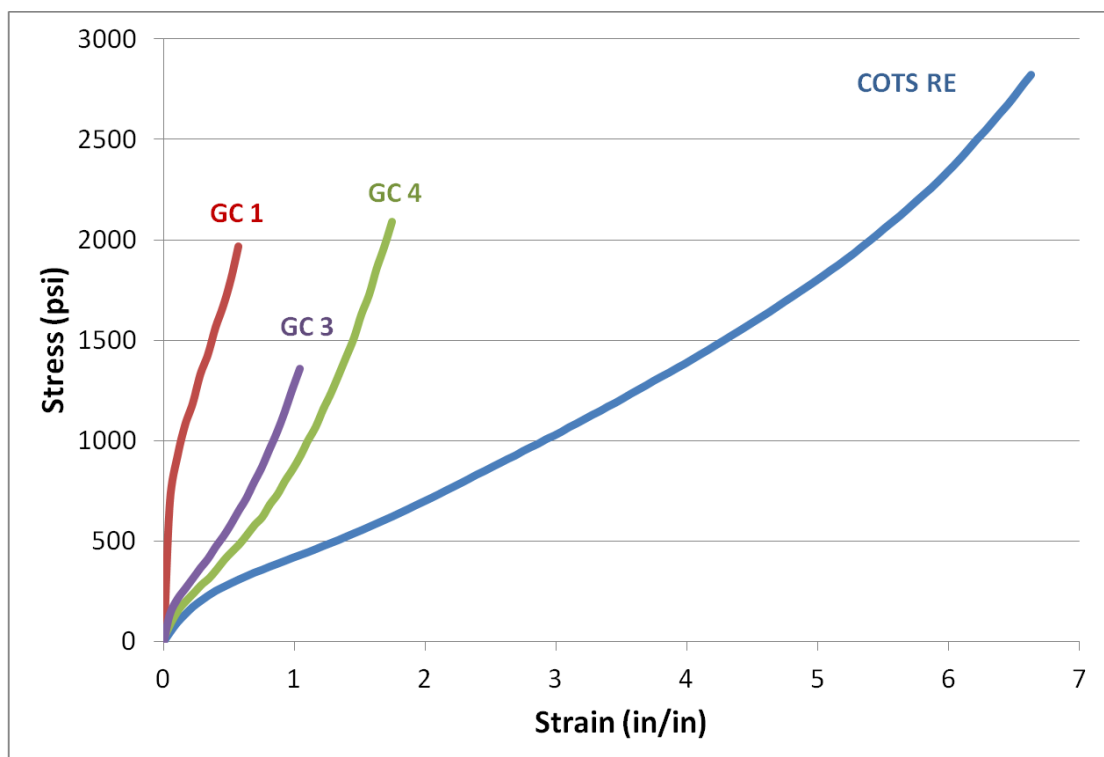
improved performance over the base GC 4 topcoat. The GC 4 with a 3 wt% loading of the aerogel additive also showed improved cavitation erosion resistance in previous testing, but were only capable of passing 8 minutes of rain erosion testing. Finally, the GC 1 topcoat with a 6 wt% loading of the rubber additive showed improved performance over previous GC 1 additive-free coatings, but did not drastically improve the rain erosion resistance.



**Figure 17. Second round of rain erosion testing at AFRL's Rain Erosion Test Facility.** Testing was conducted on Luna's GC 4 topcoat with the PreKote pretreatment and various loadings of the amine terminated rubber additive (3-9 wt %) and the aerogel additive (3 wt %). An additional GC 4 topcoat was evaluated with the COTS wash primer. GC topcoats were evaluated against the COTS RE coating.

Tensile testing in accordance with ASTM D2370 was performed on free film coatings of the GC variants and the COTS RE coating and was used to compare mechanical properties against the COTS RE coating. Figure 18 shows the results of tensile testing on the GC 1, GC 3, and GC 4 topcoats as well the COTS RE. GC 2 was not evaluated due to poor performance in rain erosion testing. The ultimate tensile strength (UTS) of the three GC topcoat variants, the stress at which the coatings fail under tension, was between 1400 and 2200 psi on average while the elongation at break (UTS) ranged from 50% to 120%. The GC 4 topcoat system was the best performing coating with the UTS and greatest elongation. The average UTS of the COTS RE was 2700 psi with an elongation at break of >600%.





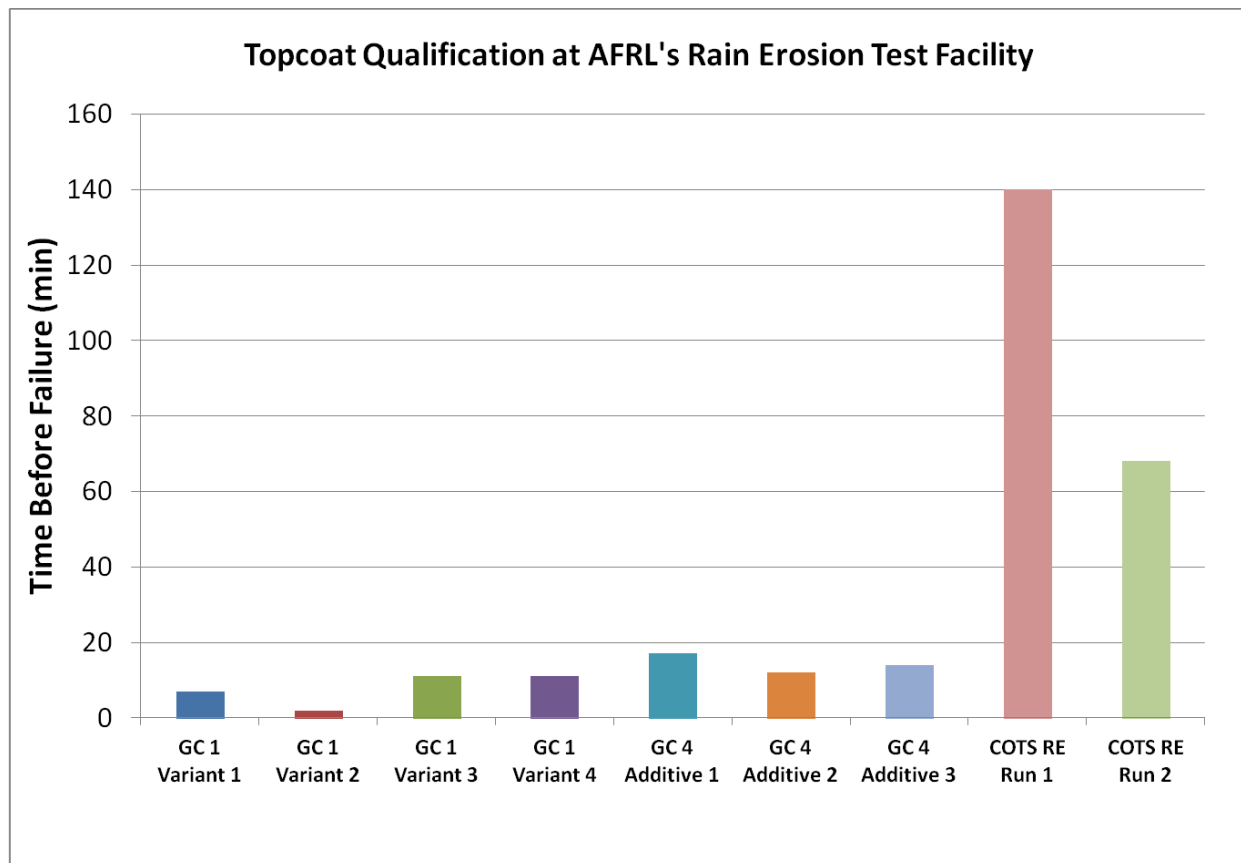
**Figure 18. Tensile testing results of Luna's GC 1, GC 3, and GC 4 topcoats and the COTS RE coating. Testing was conducted on free film coatings of the GC variants and the COTS RE at a strain rate of 10 in/min.**

Luna conducted a final round of rain erosion testing at the end of the limited scope program (Figure 19). Formulations based on the GC 1 and GC 4 base topcoat formulations were prepared with the addition of two modified amine curative packages and the additive of either a CB or SiC toughening agent. Two separate epoxy curatives, including a silanated amine and a small molecule or oligomeric amine, were evaluated as potential drop-in additives to replace the current amine curative. Additionally, the CB and SiC additives were incorporated to increase the strength and toughness of the final coatings in combination with the updated solvent packages. For this final round of testing, Luna investigated four GC 1 topcoat variants and four GC 4 variants. Once again, no resin/amine/additive combination was capable of passing more than 20 minutes of rain erosion testing on the AFRL rain erosion test apparatus, with a single GC 4 formulation being the best performing candidate material thus far (passing 17 minutes).

Luna evaluated the mechanical properties of the coating used in the final round of rain erosion testing. Several variants of the GC 4 resin, with both drop-in amine curative additives, showed a drastic increase in UTS, reaching >3000 psi in several formulations. Additionally, the elongation at break of these updated resin systems was shown to >180%. While these mechanical properties are still limited in comparison to the COTS RE, they do show promise in altering the GC topcoat formulation for improved mechanical properties and potentially improve rain erosion resistance.

Luna tested a final round of airfoil coupons of the COTS RE coating. For this effort, a new batch of the COTS RE coating system was purchased from the manufacturer and applied according to the manufacturer's recommended methods. During this coating effort, the COTS RE coating showed no signs of "popping" or blister and was free of any pre-existing defect. During this

round of testing, the COTS RE coating was capable of passing 60 minutes in one trial and up to 140 minutes in another, indicating the high level of performance in the COTS RE, but also the wide variability in data during full-scale rain erosion testing. More rain erosion testing will be required to determine if the COTS coating can meet the specified 150-180 minutes of rain erosion resistance time under SAE AMS-C-83231A conditions.



**Figure 19. Final round of rain erosion qualification at AFRL's Rain Erosion Test Facility. Testing was conducted on Luna's GC 1 and GC 4 topcoats with modified amine curative packages. GC topcoats were evaluated against the COTS RE coating.**

#### **5.4 Task 4 – Next-Step Planning**

The Luna team understands that proof-of-concept is the ultimate measure of success in a SERDP limited scope program. The rain erosion topcoats developed in this program possessed unique properties in terms of impact resistance, flexibility, and adhesion. Coatings contained no free isocyanates or HAPs and possessed VOC levels of ~150 g/L. While the Luna team was able to develop topcoat formulations with the potential of reduced environmental hazards, the coatings did not meet the rain erosion performance of SAE AMS-C-83231A. With improved performance in mechanical properties and rain erosion resistance, Luna's low-VOC rain erosion coating product may find utility in the growing environmentally friendly materials coatings sector.

Many rain erosion protective coatings, such as the CAAP and Hontek product lines, contain greater VOC levels than allowed in MIL-PRF-32239A and MIL-PRF-85322C (>340 g/L), and are considered specialty coatings with permissible use only in controlled areas on aircraft. Luna's

current GC resin formulations have a low VOC content, are non-HAPs, and do not contain any free isocyanates. These attributes would reduce the need for special permissions or exempt status. This lower VOC content would also provide a safer environment for applicators as well as reductions in fines and exhaust scrubbing requirements.

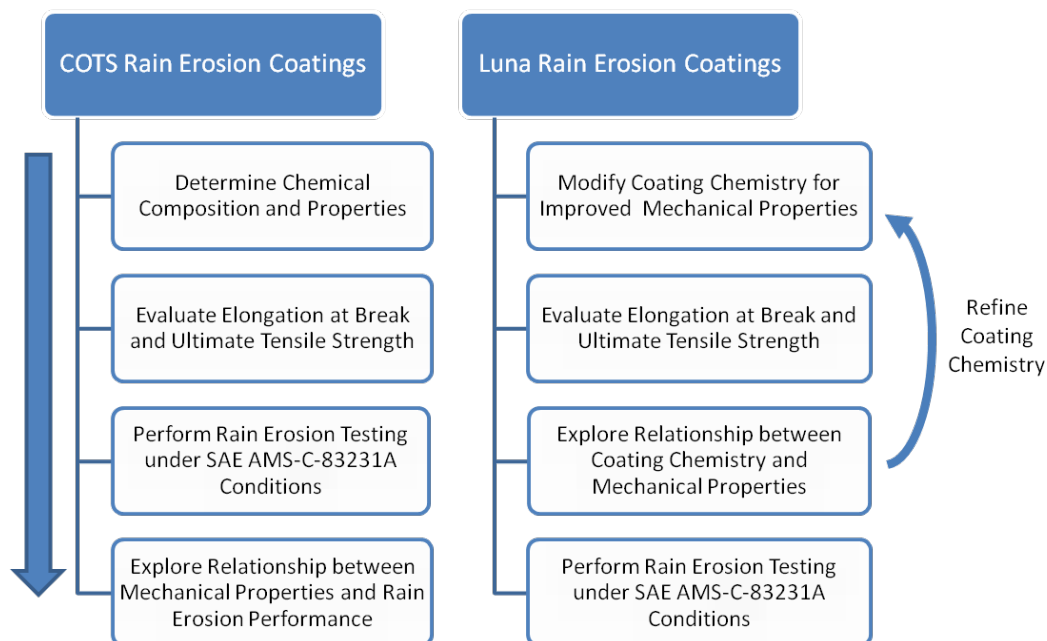
To further reduce the VOC content, Luna plans to investigate higher solids contents in the resin (Part A) and curative (Part B) components, decreased formulation viscosities, and reduced solvent loadings for spray application. Luna will pursue a variety of solvents to maximize solvent activity (i.e. higher dispersion in lower quantities of solvent), which will help dissolve resin components in the Part A and Part B sides at lower solvent loading levels. Solvent package optimization will also focus on quantifying emissions reductions at the depot level and will provide a better understanding of how a variety of solvents can improve coating performance and limit the risks associated with VOC exemption status (i.e. as exempt solvents are removed or added according to regulations, coating formulations can be adapted).

There are additional areas that Luna would like to address in a possible subsequent follow-on effort from SERDP. While the rain erosion coating product that results from follow-on funding would benefit SERDP and the DOD with an environmentally friendly, low-VOC coating system, the mechanical strength (UTS), elongation, and rain erosion performance issues as well as the cradle-to-grave sustainability, safety and environmental aspects need to be further explored. There is a critical need to understand the importance of coating chemistry (functionality, polymer structure, molecular weight, crosslinking) and how it affects the underlying mechanical properties and rain erosion performance of COTS products. Several COTS coating systems provide excellent mechanical properties that assist in meeting the requirements of a qualified rain erosion coating system. For example, the CAAP B-274 coating system is capable of an elongation at break greater than 600% with an UTS above 3000 psi. Several Hontek rain erosion coating systems provide an elongation at break of greater than 500% with an UTS as high as 7000 psi. These two mechanical properties, as well as hardness, are directly related to the rain erosion performance of the final COTS coating systems. To understand why these COTS coatings have good rain erosion performance, Luna will include in the follow-on effort an investigation of COTS coating composition as related to their mechanical and rain erosion properties.

Luna's proposed process for evaluating COTS rain erosion coatings and developing a low VOC, non-HAPs, and isocyanate free coating system is shown in Figure 20. This process will provide a pathway for developing new coatings that can meet both the environmental and performance requirements necessary for DoD weapons platforms. Early in a follow-on funding effort, Luna will investigate the chemical composition of several COTS rain erosion coatings and will evaluate their mechanical properties, including elongation at break, hardness, and UTS. The COTS coatings will be tested under SAE AMS-C-83231A rain erosion conditions at UDRI/AFRL and a relationship between their chemical composition, mechanical properties, and rain erosion performance will be used to develop performance criteria for coating development at Luna.

Once the required properties are better understood, Luna will modify the current resin coating chemistries to meet or exceed the mechanical properties of the best performing COTS products (Figure 20). Derivatives of this program's resins will be tested for elongation at break, hardness, and UTS, and a relationship between coating chemistry (composition, functionality, MW, cross-linking) and the resulting mechanical properties will be used to refine resins for improved

mechanical performance. As new coatings are down selected, testing at UDRI/AFRL under SAE AMS-C-83231A conditions will be performed to determine the overall rain erosion performance. By utilizing mechanical testing early in the program, Luna will avoid the need for numerous runs of costly rain erosion testing.



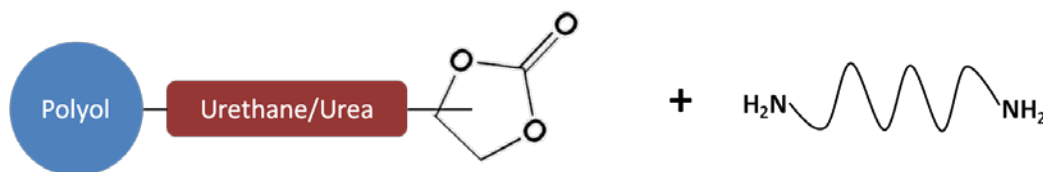
**Figure 20. Luna’s process for evaluating COTS rain erosion coatings will provide an understanding of the mechanical properties needed to qualify under SAE AMS-C-83231A testing. By refining resin chemistry and coating formulations, Luna will optimize new resin systems to meet or exceed the mechanical properties and rain erosion performance of the COTS products.**

Luna plans to address the mechanical and rain erosion deficiencies of the resins developed under this program by modifying the underlying polymer chemistry and end group functionality for improved flexibility/elongation and strength as well as the amine curative package. In terms of UTS and elongation at break, Luna will work to incorporate functional molecules into the new resin structure that have increased hydrogen bonding capabilities through the use of aromatic materials (pi-pi bonding). Additionally, urea linkages will be incorporated into the resin chemistry to further improve hydrogen bonding, increase coating mechanical properties (elongation and UTS), improve flexibility, and increase the number of hard segments in the resin backbone.

At the end of the limited scope program, Luna identified the GC epoxy functionality as a limitation in mechanical performance, as the epoxy end group removes the ability to incorporate urea linkages and decreases the overall mechanical properties and rain erosion performance. In traditional urethane reactions, a diisocyanate is reacted with a diol (hydroxy functionality), resulting in a flexible polymer with a high concentration of soft segments. A similar reaction occurs during Luna’ GC resin synthesis (Figure 2), where the isocyanate terminated polyol is reacted with the hydroxy terminated glycidol. To improve hydrolytic stability, flexibility, elongation at break and UTS in urethane type coatings, diisocyanates can alternatively be reacted with an amine curative that results in improved elongation and mechanical properties. The resulting isocyanate-amine produces urea hard segments that help to increase hydrogen bonding,

improve toughness, and amplify overall mechanical properties. The isocyanate-glycidol linkage in Luna's GC resins prevents a reaction between the isocyanate linkage and the final amine curative, inhibiting the incorporation of urea hard segments into the GC coating system. Additionally, the reaction between the epoxy end group and final amine curative results in numerous polyether segments, and the amine can further react with additional epoxy end groups increasing cross-link density.

To further improve the performance of the resins developed under this effort, Luna will investigate carbonate end group functionality (Figure 21). An initial reaction between the isocyanate terminated polyol and a small molecule amine (single functional group) will result in a prepolymer with both urethane and urea segments (hard and soft). The resulting prepolymer will then be end capped with a carbonate functional group, locking in the initial urethane/urea segment. In Luna's current GC resins, the final epoxy-amine reaction results in a polyether segment that is susceptible to hydrolytic degradation and a potential loss in mechanical properties under rain erosion conditions. With the proposed carbonate end group, the final reaction with an amine curative will result in additional urethane groups that contribute to improved hydrolytic stability, overall flexibility, and mechanical strength.



**Figure 21. Luna's proposed carbonate functionalized resins.**

Luna will also work to improve the mechanical and rain erosion properties by continuing to modify the amine curative package in final resin formulations. At the end of this program, Luna had success in improving the UTS and elongation of the GC topcoats through simple modifications to the amine curative package (drop in additives). Through the evaluation of additional curatives, Luna will modify the hydrogen bonding capabilities and amine segments to improve the new coating's toughness, elastic modulus, and elongation. This can be accomplished through modifications to the amine curative MW and functionality (primary vs. secondary), the overall chemical structure of the amine and the amine equivalent weight, and the chemical composition and hydrogen bonding capabilities of unreacted amine functional groups (or urea groups) in the curative's backbone structure.

Several materials and procedures need to be evaluated further to ensure safety and sustainability in synthesis, production and long-term procurement. All of Luna's current polyol precursors are commercially available products that are produced at the 55-gallon drum quantity or greater. These materials are common precursors for a variety of coating and polymer products on the global scale and are readily available. While Luna is focused on a low-VOC and non-HAPS rain erosion coating system, there exists some safety and environmental considerations associated with the GC resin synthesis beyond these precursors. Of particular interest is the use of diisocyanates and glycidol, both of which have the potential to be prohibited in the near future under the Prohibited and Controlled Chemical List (PCCL), OSHA regulations or the European Union's REACH program. Additional EPA regulations, such as the Toxic Substances Control Act (TSCA), must also be addressed as the use of isocyanates and glycidol may be further regulated in future revisions. While diisocyanates and glycidol are commercially available

products, these substances pose risks for manufacturers and their operators during the synthesis. In a subsequent follow-on SERDP program, Luna plans to evaluate these potentially hazardous materials and how they factor into the overall sustainability and environmental mitigation goals of SERDP, the DOD, and federal regulatory bodies. A complete hazardous operations (HAZOP) or chemical risks evaluation will be completed with the potential to work with a DOD partner, such as the Air Force Research Laboratory, or an industry regulator, to evaluate any production, manufacturing or scale-up risks.

Luna intends to collaborate in a possible subsequent SERDP program with North Dakota State University (NDSU), Luna's partner on the Air Force Phase I SBIR (FA8650-16-M-5063). NDSU is an expert in the field of polymers, coatings, and coating resins. In addition, they are the originator of the first GC resins and hold several patents in this area. Luna will work with Professor Dean Webster to modify the current resin chemistry to include urethane/urea hard segments with a carbonate functional end group. Dr. Webster will assist in developing isocyanate free chemistries at the production level and develop new synthesis procedures for a modified resin system. NDSU's expertise in resin modification will be used to refine resin components (polyol, reactants, carbonate end groups) to improve the overall chemical composition of the resulting resin for increased mechanical performance. To further the sustainability and reduce production and environmental risks, Luna and NDSU will evaluate alternative methods for synthesizing resins. Currently, the synthesis process involves a urethane reaction (isocyanate – polyol/hydroxyl) followed by epoxy end capping (glycidol) through an additional urethane reaction. Luna and NDSU have already initiated the process of developing new and innovative ways to synthesize resins while eliminating the use of the isocyanate materials.

Luna and NDSU will optimize resin chemistries to remove the need for isocyanate reactants. The most viable synthesis route, one that does not introduce additional risks or sustainability questions, is the use of a carbonate procedure. In this route, the polyol precursor, which is hydroxyl terminated, is end capped with an amine group through alkylation with ammonia. The subsequent amine terminated precursor can then be reacted, through transamidation, with the use of an appropriate polycyclic carbonate species, resulting in the release of small quantities of CO<sub>2</sub>. The carbonate functionalized precursor can then be reacted with an amine terminated component to produce a urethane/urea segment, followed by the addition of a carbonate functional group, which is inherently safer compared to glycidol. This production route eliminates the need for isocyanates and only introduces one byproduct, CO<sub>2</sub>, which introduces minimal risks due to the small quantities generated. Through synthesis evaluation and alternative resin production routes, Luna and NDSU will be capable of producing more sustainable and environmentally safe resins and the cradle-to-grave environmental risks of VOCs, HAPs, isocyanates and other potentially harmful components can be eliminated.

## **6.0 Conclusions and Implications for Future Research**

During the limited scope program, Luna was able to accomplish numerous tasks including the demonstration of several GC based topcoat variants that showed high levels of flexibility in GE reverse impact and low temperature mandrel bend testing as well as excellent dry and wet adhesion. All coatings were formulated to contain low levels of VOCs and were both isocyanate and HAPS free. Luna evaluated four GC resins with high solids content and low levels of VOC contributing solvents, demonstrated kilogram scale production of all four GC resins, and was

able to vary the GC composition and synthesis route to reduce resin viscosity and increase flexibility.

Luna tested over 50 GC topcoat variants using GE reverse impact testing, low temperature mandrel bend flexibility, and both dry and wet adhesion. Luna evaluated several different amine curative packages as well as several drop-in amine curative additives and several of these systems resulted in improved mechanical properties of the GC coatings. Both organic and inorganic fillers were also incorporated to improve the performance and strength of the GC topcoats with several variants showing improved performance over the base GC resin coatings. Over 30 of these coating variants were down selected and evaluated for mechanical performance with 18 coatings systems being tested on the full-scale rain erosion testing apparatus at AFRL/UDRI. While the developmental GC coatings did not perform as well as traditional high-VOC rain erosion coatings during rain erosion and tensile testing, the program demonstrated that there is significant room to create GC-based environmentally-friendly rain erosion systems and reduce risk associated with hazardous materials during coating application.

Increasing rain erosion performance of Luna's GC coatings is a primary objective of future work and will drive down life cycle costs in terms of operational readiness. By improving on commercially available rain erosion coatings, Luna can provide a means for reducing long-term (>10 years) life cycle costs associated with coatings removal and replacement as well as reducing the risks for complete replacement of weapons systems components. Additionally, Luna's rain erosion coatings can be applied faster and at higher build rates due to the high solids content and optimized solvent package. This increased rate of application will significantly reduce applicator time and life cycle costs while increasing turnaround and operational readiness of aircraft and their components. Finally, the reduction in VOC levels and the elimination of HAPs in Luna's GC based rain erosion formulations will provide an immediate return on investment in terms of environmental control and life cycle costs (<4 years). Luna's low-VOC coating technology will provide the means for pollution and waste reduction at both the OEM and depot level, with the majority of this reduction occurring through decreased VOC emissions to the atmosphere or exhaust filtration units and through a reduction in VOCs and HAPs in solid or liquid waste streams. Luna's GC resin formulations contain approximately 1/3 of the currently allowable VOC levels per military specifications (MIL-PRF-32239A, MIL-PRF-85322C) and 1/3 and 1/6 of the VOC content of COTS RE rain erosion coating. Without considering the performance of the coating, this reduction in VOC levels alone will drastically reduce life cycle costs from an environmental viewpoint.

In a follow-on effort, Luna would like to investigate 1) the properties of COTS rain erosion coating systems, 2) the required chemistries and mechanical properties for increased rain erosion performance, 3) the evaluation of suitable solvent packages for reduced solvent coating systems, and 4) the development of a new resin class comprised of a urethane/urea segment and a functionalized carbonate end group (resulting in an additional urethane segment when reacted with an amine curative). For this effort, Luna proposes follow-on funding in the form of an additional one year, \$150,000 limited scope program. Due to the high risk, high reward nature of the resin development process, the proposed follow-on funding would allow for additional time to demonstrate proof of concept and would allow Luna the opportunity to systematically investigate the properties required for rain erosion resistance in DoD applications.

With follow-on funding and optimization of the rain erosion coatings, the return-on-investment (ROI) for SERDP and the DoD agencies (e.g. the USAF) in terms of lowered sustainment and

environmental costs associated with radome protective coatings on aircraft will be significant. This is associated with the large quantity of USAF and Navy aircraft radomes and antennas processed annually at maintenance depots. Other commercial markets include leading edges of military and civilian aircraft wings, hypersonic missiles, lift rockets and spacecraft, wind turbine blades, and helicopter blade leading edges. The application market is thus extremely widespread for the developed technology.



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## APPENDIX A

### Key Metrics from SAE AMS-C-83231A and MIL-PRF-32239

**Table 5: Critical Performance Properties (ref: SAE-AMS-C-83231A)**

Material Property	Test Method	Target Criteria	Substrate
Peel Strength	Following complete cure, 2-1" wide strips shall be cut lengthwise through the coating. The material will be peeled back at a 180° pull at 2 in/minute	7 pounds per inch	Composite
Flexibility	Conditioned at -54 °C (-65 °F) for 1 hour then bent over 1/8" mandrel per Fed Std 141 Method 6223	No cracking or loss of adhesion	2024-O anodized
Water Resistance	Immersion in distilled water for 24 hours at standard conditions. The exposed coupons will be tested for visual appearance and peel.	No evidence of blistering, swelling, checking or visible color change. Peel strength shall not be below 7 pounds/in	Composite
Aromatic Fuel Resistance	Immersion in ASTM D471 Fuel B for 1 hour. The exposed coupons will be tested for visual appearance and peel	No evidence of blistering, swelling, checking or visible color change. Peel strength shall not be below 7 pounds/in	Composite
Rain Erosion Resistance	Placed on propeller blade and spun at 500MPH in specialized rain erosion test rig.	No Erosion through a 0.012 to 0.014" coating after 150 minute (minimum) and 180 minute (goal)	Composite Air Foils
Electrical Transmission	Transmission efficiency of microwave power tested between several points on coated substrate.	Min electrical transmission of 85, 90 or 95 %	Composite
Surface Resistivity	500-volt megohmmeter used to measure resistivity between several points on coated substrate.	No less than 0.5 megohms nor more than 15 megohms per square	Composite
Weather Resistance	Continuous outdoor weathering for 6 months	No signs of film deterioration such as: chalking, checking, cracking, embrittlement, loss of adhesion or loss of resiliency	Composite
Strippability	Strippable using laser, Flashjet or approved chemical stripper.	Strippable	Composite

**Table 6: Additional Desired Performance Properties (ref: MIL-PRF-32239)**

<b>Property</b>	<b>Test Method</b>	<b>Target Criteria</b>	<b>Substrate</b>
Weather Resistance	Exposure for 3000hrs in a Xenon-Arc chamber that is cycling between 102 minutes of light only and 18 minutes of light and DI water spray	Color change $\Delta E \leq 1$ Adhesion $\geq 4B$ GE Impact Flexibility $\geq 10\%$	Composite Composite 2024-O anodized
Lubricating Oil Resistance	MIL-PRF-23699: Immersion in lube oil for 24 hours at $250 \pm 5^\circ F$	The coating shall not exhibit any blistering, softening, or other coating defects. Slight staining of the coating is acceptable	Composite
Hydraulic Fluid Resistance (MIL-PRF-83282 & Skydrol)	MIL-PRF-83282: Immersion in hydraulic fluid for 24 hours at $150 \pm 5^\circ F$ ; Skydrol: Ref. MIL-PRF-32239 (AF Coating System Specification)	The coating shall not exhibit any blistering, softening, or other coating defects. Slight staining of the coating is acceptable	Composite